Experimental report

27/04/2019

Proposal: 6-06-479 **Council:** 4/2017

Title: Neutron powder diffraction study of fluorinated graphites

Research area: Materials

This proposal is a new proposal

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Samples: Graphite
CF
C2F
C4F
CF - defluorinated
C2F defluorinated

Instrument	Requested days	Allocated days	From	To
D4	3	3	25/05/2018	28/05/2018

Abstract:

Fluorine-graphite compounds (CxF) are very interesting for their potential applications as cathode materials in primary batteries. The nature and strength of the C-F bonding change from ionic to semi-covalent up to pure covalent, as the degree of fluorination increases and this results in a dramatic change of the structure and physical properties, in particular of the electronic band structure. We propose to investigate the atomic structure of Fluorinated graphites at different F content by means of high energy neutron diffraction and atomic pair distribution function (PDF) data analysis using the D4 diffractometer at
the ILL.

"Neutron Powder diffraction study of fluorinated graphites"

Experimental report: number 6-06_479
Date: 25/05/2018 – 28/05/2018
Instrument: D4C
Experimental team: Chiara Cavallari (ESRF, main proposer), Vittoria Pischedda (ILM, Université Lyon 1), Silvana Radescu (University of La Laguna, Tenerife, Spain), Michela Brunelli (CRG-DUBBLE, ESRF)
Local contact: Henry Fischer

Aim of the experiment

Fluorine-graphite compounds (C_xF) appear as very interesting materials for their potential industrial applications as cathode materials in primary batteries. The nature and strength of the C-F interaction change dramatically from ionic to semi-covalent up to pure covalent, as the degree of fluorination increases. With this experiment we propose to investigate the atomic structure of fluorinated carbons at different F content by means of high energy neutron diffraction and atomic pair distribution function (PDF) data analysis using the D4C diffractometer at the ILL, in order to correlate it to the change of the structure and physical properties, in particular of the electronic band structure.

Experimental details

Our study was focused on several fluorinated carbon-based samples: the graphite-fluorides CF, C_2F, C_4F and $CF_{0.83}$, nanodiamonds obtained by detonation, nanodiamonds after fluorination treatment, fully fluorinated fullerene $C_{60}F_{48}$. Graphite powder was measured as reference too. Samples were synthetized by our collaborators (Prof. Marc Dubois, Université Clermont-Auvergne) using precursor carbon powders exposed to fluorine flux at high temperature and handled at ambient conditions afterwards [more details can be found in].
Powdery samples were load in a 5mm cylindrical Vanadium cell at ambient conditions. Two identical cells were used to collect data for all the samples.
The wavelength used was 0.5Å (refined value λ=0.4975 Å), which provides a good compromise between high neutron flux and high Q_{max} = 23.5 $Å^{-1}$, very useful for space Fourier transforms and analysis in the direct space.

Measurements were performed at room temperature in a bell jar. Stability tests, background, empty bell jar and empty cell runs for the two cells were performed. Data were then regrouped, corrected from backgrounds and inelastic contributions. The density and number density were taken into account in the data reduction and treatment. Data were treated using the D4C routines with correct program integrated therein.

Results

A direct analysis of the Real Space data was carried out for the all the samples, this giving access to the atom-atom distances r (Å) in direct space. Experimental data were used to compare with previous theoretical structural models and X-ray diffraction data collected at the beamline ID13a at the ESRF. In particular C_4F, C_2F, C_1F data together with graphite are discussed in details and shown in Fig. 1 and Fig 2. They have been reported in [*Cavallari C., Brunelli M., Radescu S., Dubois M., Batisse N., Vaughan G.B.M., Fischer H.E., Pischedda V., Carbon 147, 1-8 (2019)*], to support X-ray diffraction and electronics structures investigations of the same samples.

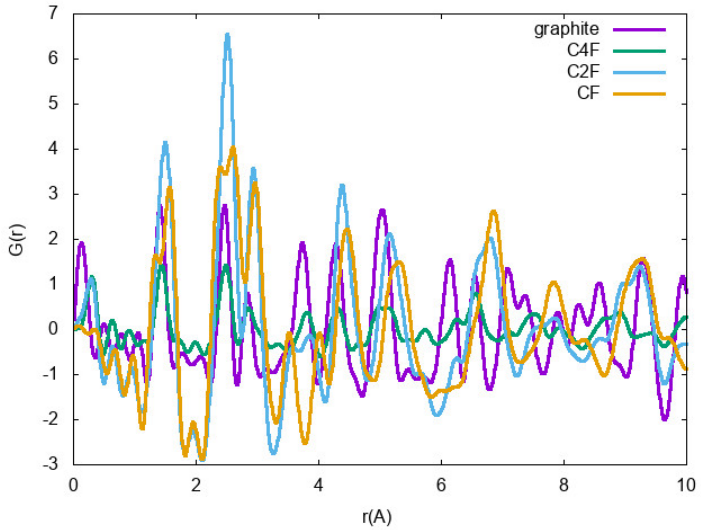

Figure 1: G(r) of fluorinated graphites: zoom up to 10 Å. Arbitrary scale along the y-axis.

Neutron data in direct space (see Fig. 1 and Fig. 2) show one single oscillation in the low *r* region of the G(*r*) of C_4F, with the first shell distances centred at 1.44 Å, slightly higher value than for graphite (pure C sp^2 system) and in fair agreement with the model discussed in [*Pischedda et al. Carbon 2018*], where F atoms bond to C atoms of the graphite planes at the same side in intercalation sequence CFCF.
For the C_2F sample, experimental data show two distances in the low *r* region of the PDF at 1.37 Å and 1.56 Å. which agree very well with the distances C-F = 1.37 Å and C-C =1.56 Å predicted by the DFT model proposed by [*Sato et al. Carbon 2004, Pischedda et al Carbon 2017*]. However, the agreement with the model is poorer at higher *r*, i.e. with the distance at 3.2 Å not reproduced in the experimental data and the model fails to reproduce satisfactorily the data above 5.8 Å. Data suggests that we are in presence of fragmented nanostructured domains of the structural models.
Finally, for the CF sample, neutron data show two distances in the low *r* region of the PDF, at 1.36 Å and 1.58 Å which are in good agreement with the distances predicted by the DFT calculated model [*Charlier et al. PRB 1993*]. Experimental data also seem to agree on second and third coordination shells. CF being the compound with the highest F/C ratio (x= 1), the proposed theoretical model is close to the observation.

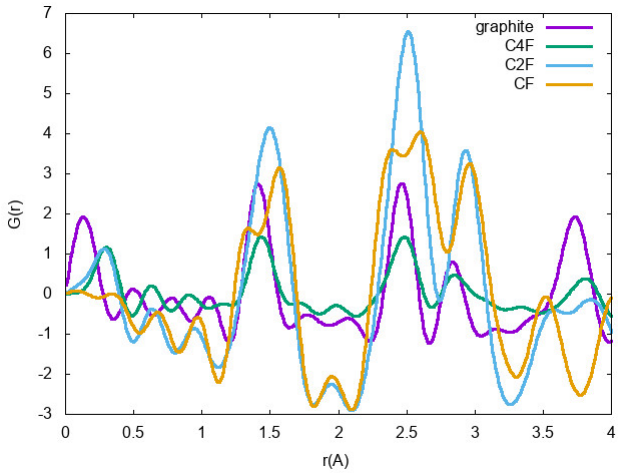

Figure 2: G(r) of fluorinated graphites: zoom up to 4 Å. Arbitrary scale along the y-axis.

Studies on the other samples are currently in progress.