# Experimental report

03/09/2015

**Proposal:** **6-06-456** **Council:** 4/2014

**Title:** High-energy neutron powder diffraction of alkali intercalated hydrofullerides

**Research area:** Materials

**This proposal is a new proposal**

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**Samples:**
$Li_{12}C_{60}D_{36}$
$Li_6C_{60}D_{36}$
$Na_{10}C_{60}D_{36}$

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D4 | 4 | 3 | 17/09/2014 | 22/09/2014 |

## Abstract:

Highly doped alkali fullerides appear particularly suitable for developing efficient hydrogen storage systems. Nevertheless, the precise knowledge of the hydrogenation mechanism is still missing in these compounds, due to the high degree of crystalline disorder, which prevented so far their detailed structural investigation. Here we propose to investigate the morphology of such systems at the nanoscale, by means of high energy neutron diffraction and atomic pair distribution function (PDF) data analysis.

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Instrument: D4

# High-energy neutron powder diffraction of alkali intercalated hydrofullerides

## Abstract

alkali-cluster intercalated fullerides recently found renewed interest as novel materials for hydrogen storage applications, due to the high amount of reversibly chemisorbed hydrogen (up to 6 wt% $H_2$) at relative low temperature (250 – 350 °C). The absorption leads to the formation of an *fcc* or *bcc* arrangement of $C_{60}H_y$ ($18 < y < 48$, depending on the alkali metal) molecules, whose structure results distorted respect to the original $I_h$-$C_{60}$ molecule. Hence, we propose to investigate the molecular structure of $C_{60}H_y$ in the $Na_{10}C_{60}D_y$, $Li_6C_{60}D_y$ and $Li_{12}C_{60}D_y$ model compounds by means of high-energy neutron powder diffraction and atomic pair distribution function (PDF) data analysis using the D4 diffractometer at ILL.

## Aim of the experiment

Due to the lack of a structural model for $C_{60}D_y$ in such kind of compounds, it was not possible to refine neutron or synchrotron diffraction data by means of Rietveld data analysis up to now. With this experiment, we expect to extract informations about the geometry and structure of hydrogenated fullerene molecules. These will be useful to better understand the hydrogenation process and to localize the position of alkali metals, still intercalated in the *fcc* or *bcc* structure.

## Experimental details

Around 350 mg of samples were loaded in a 5 mm diameter vanadium cell. The neutron wavelength was set to 0.5003 Å (refined using a Ni standard), which provides a good compromise between the high neutron flux and the high $Q_{max} = 23.5$ Å$^{-1}$, ideal for space Fourier transforms and data analysis in the direct space.

The following samples were measured: $Na_{10}C_{60}D_y$, $Li_{12}C_{60}D_y$ and $Li_6C_{60}D_y$ (the latter was also measured in a long scan at $\lambda = 0.35$ Å). All the measurements were performed at 20 K, in order to reduce the thermal noise. Stability test, background, empty cryostat and empty cell runs were performed as well. Data were regrouped, corrected for the background and inelastic contributions. The amount of chemisorbed deuterium was previously measured in an absorption experiment and was considered in the data treatment for the calculation of the average structure factor.

## Preliminary results

The structure factor, S(Q), of deuterated fullerides is reported, as S(Q)[S(Q)-1] in Figure 1. While $Na_{10}C_{60}D_y$ crystallizes in an *fcc* structure, both $Li_6C_{60}D_y$ and $Li_{12}C_{60}D_y$ show *bcc* peaks. As expected, the presence of NaD was detected in $Na_{10}C_{60}D_y$, as well as LiD was found in $Li_6C_{60}D_y$ and $Li_{12}C_{60}Dy$ samples. Both NaD and LiD constitute a minor fraction, inevitably present as secondary phase after the absorption, and is supposed to does not significantly affect the G(r).

By Fourier transformation of the S(Q)[S(Q)-1] we extracted the pair distribution functions. These are shown and compared with the models of $C_{60}$ molecule and the most stable isomers of $C_{60}D_{36}$ in Figure 2. The G(r)'s of deuterated fullerides display remarkable differences from $C_{60}$: the first peak at ~1.1 Å is easily attributed to the C-D formed on the outer face of fullerene after hydrogenation.

Moreover, the first C-C peak moves from 1.42 to ~1.5 Å after deuteration, due to the change of hybridization from $sp^2$ to $sp^3$.

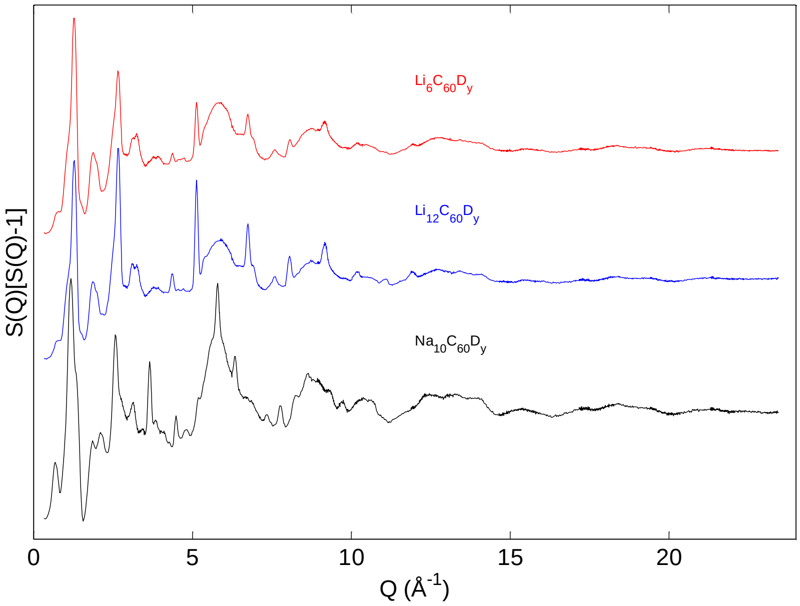

*Figure 1: S(Q)[S(Q)-1] functions of deuterated fullerides.*

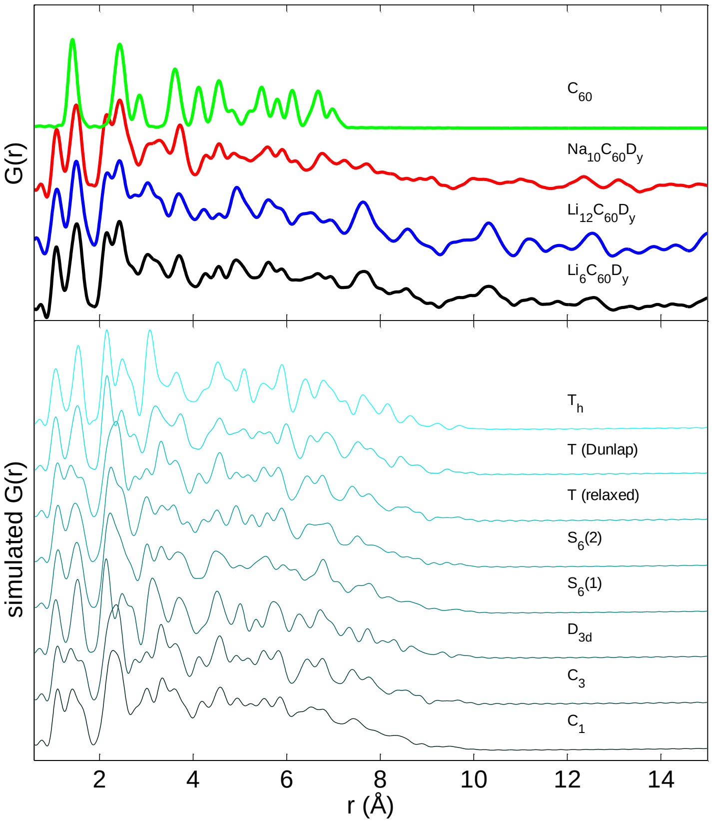

*Figure 2: extracted G(r) of samples (up) are compared with the simulated G(r) of the most stable isomers of $C_{60}D_{36}$*

Although small in amplitudes, oscillations in the G(r) after 10 Å (the mean diameter of a $C_{60}D_{36}$ molecule) suggest the presence of some intermolecular order. The comparison between the experimental data and the simulated G(r) for different $C_{60}D_{36}$ isomers suggest the formation of high symmetric isomers (e.g. $D_{3d}$, $S_6$, T, $T_h$) characterized by slight distortions. The presence of intercalated Na and Li is also expected to further complicate the analysis. The mean square analysis of these models is still in progress and will hopefully help to find the structure of deuterated fullerides, allowing to better understand the interaction of hydrogen with alkali-cluster intercalated fullerides. This analysis will be carried out by combining the neutron G(r)'s with the pair distribution functions extracted form high-energy synchrotron powder diffraction.