

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                               |                  |             |            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------|-------------|------------|
| <b>Proposal:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 7-04-125                                                                      | <b>Council:</b>  | 10/2012     |            |
| <b>Title:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Neutron spectroscopy on Sodium-Intercalated Fullerides                        |                  |             |            |
| <b>This proposal is a new proposal</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                               |                  |             |            |
| <b>Research Area:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Materials                                                                     |                  |             |            |
| <b>Main proposer:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | CAVALLARI Chiara                                                              |                  |             |            |
| <b>Experimental Team:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | BRUNELLI Michela<br>CAVALLARI Chiara                                          |                  |             |            |
| <b>Local Contact:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | JIMENEZ-RUIZ Monica<br>ROLS Stephane                                          |                  |             |            |
| <b>Samples:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Sodium intercalated fulleride Na8C60<br>Sodium intercalated fulleride Na10C60 |                  |             |            |
| <b>Instrument</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | <b>Req. Days</b>                                                              | <b>All. Days</b> | <b>From</b> | <b>To</b>  |
| IN4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 6                                                                             | 5                |             |            |
| IN1 LAG                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 6                                                                             | 6                | 02/08/2013  | 08/08/2013 |
| <b>Abstract:</b><br>Na intercalated fullerides Na <sub>x</sub> C <sub>60</sub> are nowadays intensively studied by theoreticians as systems for hydrogen storage applications. In particular decoration with alkali metals is expected to enhance the absorption capacity and reach the ideal binding energy via electrostatic interaction between molecular hydrogen and charged fullerenes. We recently managed to synthesize Na <sub>10</sub> C <sub>60</sub> and Na <sub>8</sub> C <sub>60</sub> and investigated the hydrogen absorption/desorption properties in Na <sub>10</sub> C <sub>60</sub> , finding a reversible 3.5 wt% H <sub>2</sub> uptake through the formation of NaH and hydrogenated-C <sub>60</sub> (fullerane). However, a clear understanding of hydrogen absorption mechanism as well as of the lattice dynamic modifications induced by the sodium intercalation, is still missing. Hence, we propose to investigate our samples before and after thermal treatment in hydrogen flux, by means of inelastic neutron scattering, in order to get more information about the dynamical properties of such systems. In this proposal, we require 6 days on the thermal-neutron Time-of-Flight IN4 spectrometer and 6 days on the hot-neutron two-axis Lagrange spectrometer at the ILL. |                                                                               |                  |             |            |

### **Neutron spectroscopy on Li and Na fullerenes**

We have recorded the INS spectra of  $\text{Li}_6\text{C}_{60}\text{H}_y$ ,  $\text{Li}_{12}\text{C}_{60}\text{H}_y$  and  $\text{Na}_{10}\text{C}_{60}\text{H}_y$  on the LAGRANGE spectrometer at the ILL.

Samples were obtained by solid state reaction of pure commercial  $\text{C}_{60}$  with the metal-azide and then subsequently put under hydrogen pressure (200 bar) at 200°C-400°C.

LAGRANGE is a high resolution (2%) and broad energy range (few meV – hundreds of meV depending on the used monochromator) hot neutron spectrometer, which well fits the spectroscopy of hydrogenated materials.

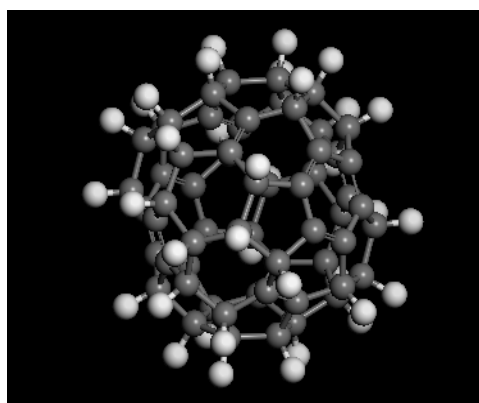
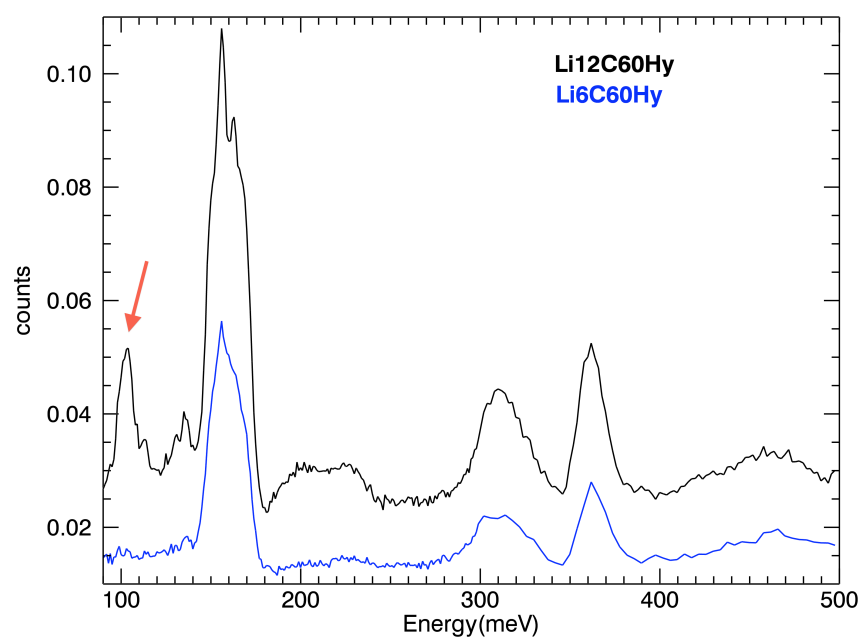
Spectra were recorded at 5K to freeze the chemistry and reduce thermal vibrations. Cu(220) and Cu (331) were used to monochromatize the incident beam, allowing an energy transfer from 27 meV to 500meV.

Previous investigation using the thermal neutron time-of-flight spectrometer IN4c (ILL) showed the existence of a broad and strong peak, located at around 150 meV for all the samples. This band is expected to originate mainly from Csp<sup>3</sup>-H bending modes, hence revealing the chemisorption of atomic hydrogen at the carbon buckyball, that took place during the hydrogenation process.

Thanks to the LAGRANGE high resolution, it has been possible to further investigate the structure of the C-H bending and stretching bands. The intensity and frequency of each peak strongly depend on the local environment of the chemisorbed hydrogen atoms.

In particular, the broad bending band located around 150 meV has been decomposed in different components, which surprisingly appear to be essentially similar for all the samples, even if additional features can be pointed out.

The combination of DFT calculations, currently in progress, and neutron spectroscopy data could allow to identify the preferential hydrogenation sites in Li and Na fullerenes and subsequently, support structural models for the hydrofullerenes.



Top: Experimental  $(S(Q, \omega))$  vs  $\omega$  (incident energy) for  $\text{H}_y\text{Li}_{12}\text{C}_{60}$  and  $\text{H}_y\text{Li}_6\text{C}_{60}$  collected on Lagrange @5K using the Cu (331) monochromator. The presence of the peak at 100K in  $\text{H}_y\text{Li}_{12}\text{C}_{60}$  (indicated with the red arrow) could be attributed to the formation of a minority phase of Li-H.  
 Bottom: One of the possible isomers of  $\text{C}_{60}\text{H}_{36}$  ( $D_{3d}$ ) – Hall 1993