Experimental report

15/11/2016

Proposal:	**7-01-430**	**Council:**	4/2015
Title:	Temperature dependence of lattice dynamics in $Li_{12}C_{60}$		
Research area:	Materials		

This proposal is a new proposal

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Samples: $Li_{12}C_{60}$

Instrument	Requested days	Allocated days	From	To
IN4	5	4	12/11/2015	16/11/2015

Abstract:

The Li-intercalated fulleride $Li_{12}C_{60}$ has shown interesting properties for potential applications in the field of hydrogen and energy storage. In the pseudo-cubic structure, C_{60} units keep their molecular character and small Li cubic clusters are placed in the voids of the parent host lattice. Recent investigations, including uSR, INS and ab-initio lattice calculations have shed light on the hydrogenation process and evidenced a lithia rearrangement for temperatures above 150 K. We would like to complete this study by performing a temperature analysis of the lattice modes, as measured on IN4C from 10 K to 320 K. For this experiment, we require 5 days on IN4C.

EXPERIMENTAL REPORT

Title: Temperature dependence of lattice dynamics in $Li_{12}C_{60}$

N: exp 7-01-430

Instrument: IN4C

Dates: 12-16/11/2015

Sample: Li-intercalated fulleride Li12C60, m=0.295 g

Experimental details: wavelength: λ=2.22 Å, temperature range (standard Orange cryostat): from 320 K to 10 K, sample holder: flat rectangular Al-cell with In o-ring and Cd mask, sample loading in Ar-glove box (O_2 and H_2O content < 0.1 ppm) to prevent any possible oxygen, moisture contamination of the sample.

Scientific motivation: Lithium-intercalated fulleride at high stoichiometry $Li_{12}C_{60}$ has been recently investigated thanks to its hydrogen storage and high ionic conductivity properties [1]. Due to the high Lithium content, C_{60} retains its monomeric structure and the intercalant atoms form small clusters confined into the voids of the crystalline host phase.
$Li_{12}C_{60}$ has proved to reversibly uptake hydrogen via a complex H-chemisorption mechanism, supported by the implication of the Li tetrahedral clusters. In addition, previous μSR and INS data have evidenced a thermal dependence of the Li-dynamics, which is compatible with an activated Li-clusters rearrangement with an onset temperature of 150 K [2]. The aim of the proposed experiment was to investigate the Li-modes in the [10-25 meV] range between 10 K and 320 K to shed a brighter light on the dynamical properties of $Li_{12}C_{60}$

Results:

Fig. 1 shows the evolution of the GDOS as a function of temperature. Dataset have been collected at 8 different temperature from 10 K to 320 K. Only the most meaningful data at 100 K, 200 K, 250 K, 320 K is reported here for clarity. Previous *ab-initio* calculations of the dynamics and experimental data collected at IN4C using incident neutrons of λ=1.11 Å (reported in ref. [1]) showed that Lithia modes dominates the total spectrum in the "C_{60} gap" region, i.e. 10–27 meV, with predominant contribution at 15 and 22 meV. Indeed, this energy range including the lower [3 – 10 meV] region, is strongly affected by temperature, with a consistent increase of intensity in particular at 250 K. This increase in the GDOS dominated by Li vibrational modes appears related to a progressive broadening of the elastic line that could originate from single-particle motion in the ps time scale. Further data analysis, most likely accompanied by DFT-simulations, is needed to shed more light into the dynamical process originating the features observed.

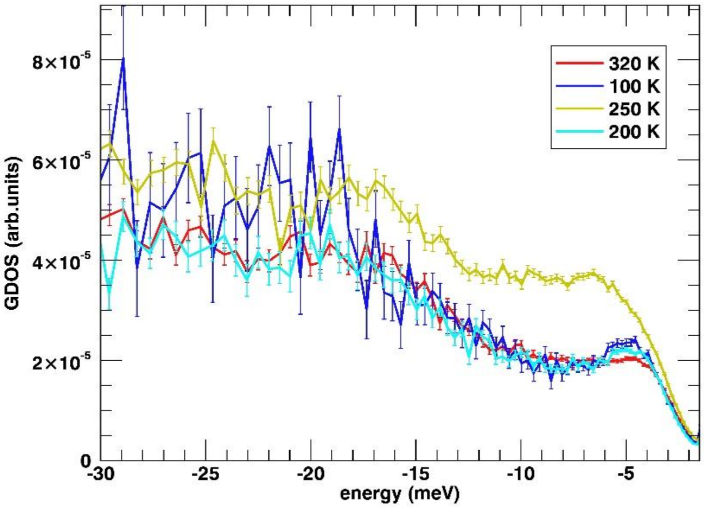

Figure 1 : GDOS of Li12C60 measured at 100 K, 200 K, 250 K and 320 K. Energy range from [0; 30 meV] is plotted

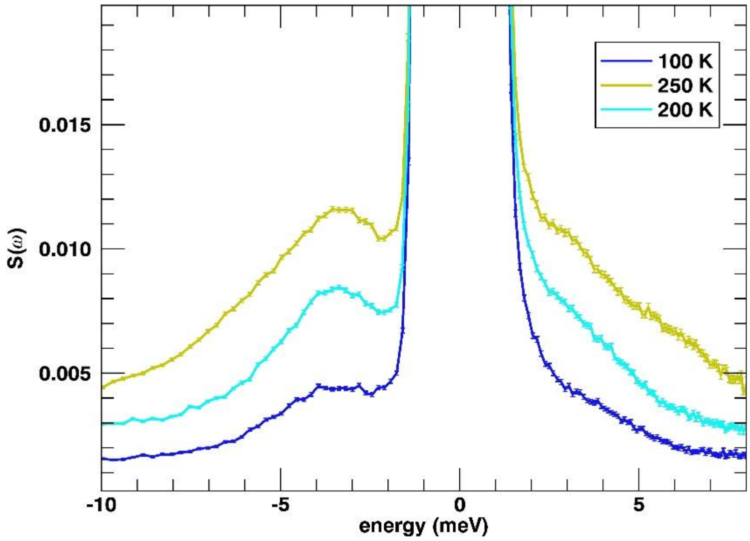

Figure 2: Susceptibility of Li12C60 as a function of temperature measured on IN4C.

References:

[1] Hydrogen sortion in Li12C60 – Mauron Ph. et al. – JPPC 2013, 117 (44), 22598–22602

[2] Hydrogen storage mechanism and lithium dynamics in Li12C60 investigated by μSR – Gaboardi M. et al. , Carbon 90 (2015) 130-137