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ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*http://193.49.43.2:8080/smis/servlet/UserUtils?start*

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

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|---|---|---|
| ESRF | **Experiment title:**<br>Structural investigation of the expanded phases of $Mg_xC_{60}$ with THF ($1 \leq x \leq 5$) | **Experiment number**:<br>CH- 3490 |
| **Beamline**:<br>ID31 | **Date of experiment**:<br>from: 26.10.2011 to: 28.10.2011 | **Date of report**:<br>01.03.2012<br>*Received at ESRF:* |
| **Shifts:**<br>6 | **Local contact(s)**:<br>Dr. Andy Fitch | |

**Names and affiliations of applicants** (* indicates experimentalists):

**Dr Daniele PONTIROLI***

## Report:

It is well known that magnesium cannot be intercalated easily in carbon based compounds, as for example in graphite [1]. On the contrary, solid fullerene can host up to 5 Mg atoms per $C_{60}$ in the lattice interstices, where $C_{60}$ molecules polymerise to form a 2D rhombohedral structure with metallic character and unexpected thermal stability [2]. Recently, we also managed to isolate a new Mg fulleride $Mg_2C_{60}$, through a direct solid state reaction. Synchrotron and neutron powder diffraction, performed respectively at ID31 (ESRF, Grenoble) and at HRPT (SINQ-PSI, Villigen) proved that $Mg_2C_{60}$ shares the same structure of the superionic conductor $Li_4C_{60}$, with a peculiar hybrid 2D bonding network [3].

Magnesium intercalated fullerides represent interesting systems, which could find applications in the field of energy storage, as electrodes for future Mg-ion batteries or as materials for the accumulation of hydrogen in solid state tanks [4].

In order to optimise the intercalation process and also to possibly extend the family of Mg intercalated fullerene compounds, recently we explored new chemical routes for the synthesis of these systems. In particular, we managed to intercalate $C_{60}$ with Mg via a “cold” reaction mediated by solvents, in which the alkali-earth metal can enter in solution, such as ammonia, tetrahydrofuran (THF) and methylamine. While the latter gave invariably rise to amorphous compounds, stable crystalline samples were indeed produced by using ammonia and THF.

High resolution synchrotron radiation diffraction was performed at the beamline ID31 ($\lambda = 0.40006$ Å) on several Mg intercalated fullerides, obtained from different reaction mediated by solvents, either THF and ammonia. While in the case of THF data substantially confirmed the previous results extracted by diffractograms collected at BM1B (see experimental report of experiment CH-3258), in which $C_{60}$ units are packed in a hexagonal lattice in which THF molecules are co-intercalated (see Figure 1a)), samples obtained from reaction in liquid ammonia displayed a quite different crystalline arrangement.

Diffraction pattern collected at room temperature on the sample with the nominal stoichiometry $Mg_4C_{60}$ is shown in Figure 1b). It consists of broad peaks which were easily indexed with a close packed hexagonal

cell:
S. G. *P6$_3$/m m c*, a = 10.014(1) Å, c = 16.320(3) Å, γ = 120° (Le Bail analysis).
The most intense peaks shows an unusual profile, which could not be fitted easily. However, a more careful investigation revealed that this arises from the superimposion the contributes of two phases, the hexagonal one, with broader peaks, plus another one featuring a face centered cubic cell: S. G. *F m -3 m*, a = 14.180(2) Å. A closest inspection of the cell parameters values indicated that the latter could be compatible with segregated pristine $C_{60}$, as a minority phase. Concerning the former, which approximately represents more than 90% of the sample, surprisingly it closely resembles the hexagonal polimorphic modification of $C_{60}$, which is known to be thermodinamically unstable under normal conditions; it could be obtained, for example, upon crystallizing from fullerene solutions frozen with liquid nitrogen [5].
Since in this case the sample was obtained under normal conditions, we believe that the propensity of $C_{60}$ units to arrange in a hexagonal lattice is rather induced by the presence of Mg. The slightly shorter lattice parameters in our sample, if compared with those of hexagonal $C_{60}$ (a ~ 10.02 Å and c ~ 16.38 Å) suggests the possible intercalation of Mg ions in the observed structure, although further structural analysis (Rietveld refinement), still in course, will be necessary to prove it. The refined interfullerene distance is of ~ 10 Å, a value which is large enough to exclude the presence of fullerene polymerisation, but on the other hand, also too short to be compatible with the presence of co-intercalated ammonia molecules.

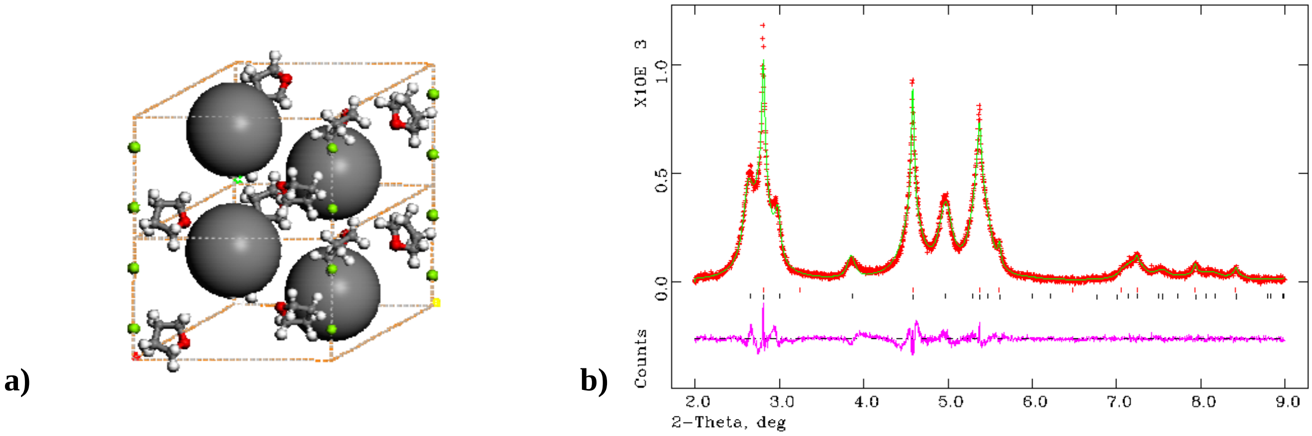

**Figure 1:** a) Proposed structure of $MgC_{60}(THF)_3$. b) Comparison of calculated and symulated powder diffraction pattern of $Mg_4C_{60}$ synthesized in liquid ammonia (Le Bail analysis, Rwp = 5.17 %)

## References

1 P. Novak, R. Imhof, O. Haas, *Electrochim. Acta* **45**, 351 (1999).
2 D. Quintavalle et al., *Phys. Rev. B* **77**, 155431 (2008).
3 D. Pontiroli, M. Aramini, M. Gaboardi, M. mazzani, A. Gorreri, M. Riccò, I. Margiolaki and D. Sheptyakov, *Carbon*, manuscript submitted.
4 L. Schlapbach and A. Zuettel, *Nature* **414**, 353 (2001).
5 E. V. Skokan et al., *Carbon* **43**, 803 (2005).