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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

Reports supporting requests for additional beam time

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.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

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.

  ESRF	**Experiment title:** Structural investigation of the polymer phases of Mg_xC_{60} compounds (2≤x≤6)	**Experiment number**: CH- 3258
Beamline: BM1B	**Date of experiment**: from: 23.09.2010 to: 27.09.2010	**Date of report**: 18.02.2011
Shifts: 9	**Local contact(s)**: Dr. Wouter Van Beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Daniele PONTIROLI*

Report:

It is known that magnesium cannot be intercalated easily in carbon based compounds, like 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 [3]. Synchrotron powder diffraction at ID31 proved that Mg_2C_{60} shares the same structure of the superionic conductor Li_4C_{60}, with a peculiar hybrid 2D bonding network. Diffraction scans on heating evidenced also an extraordinary thermal stability up to 800 K, while Li_4C_{60} undergoes a polymer-to-monomer transition at 600 K (see report of the experiment CH-2715). The small Mg^{2+} ions are expected to diffuse already at low temperature promoting even in this system an efficient superionic conductivity and this opens to applications in future Mg-ion batteries. Moreover, the well known ability of Mg to bind hydrogen makes this material also promising as a solid absorber of this gas.

In order to optimise the intercalation process and also to possibly extend the family of Mg intercalated fullerene compounds, recently we explored also different chemical routes.

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, as tetrahydrofuran (THF) and methylamine. While the latter gave rise to amorphous compounds, stable crystalline samples were indeed produced by using THF. Here, the solvent itself took part to the reaction and was incorporated in the crystalline structure of the product, which resulted significantly expanded as compared with the host C_{60} lattice.

In order to disentangle the structure of these new compounds, we performed high resolution synchrotron radiation powder diffraction at the beamline BM1B, both at room and at low temperature (down to 10 K), with monochromatic beam (λ = 0.5012(1) Å).

The samples were sealed in quartz capillaries of 0.5-1 mm diameter and mounted on the sticks of the helium cryostat. Technical problems found during the experiment with the apparatus for spinning the capillaries in the cryostat prevented us to properly average the effects induced by preferred orientations for some samples, and hence to obtain a reliable peak intensity in the diffractograms. However, one sample sealed in a bigger

capillary of up to 1 mm diameter which also displayed a better powder homogeneity, as checked by preliminary laboratory XRD measurements on a Bruker D8 Discovery equipped with an area detector (see Figure 1) allowed us to collect good quality data also at low temperature.

The majority of the rather narrow peaks in the diffractogram collected on the $Mg_xC_{60}(THF)_y$ sample were indexed with the hexagonal cell: S. G. *P6$_3$/m m c*, a = 15.240(1) Å, c = 9.882(1) Å, γ = 120° (see Le Bail analysis shown in Figure 2). Some strong peaks at higher 2θ angle were easily attributed to a small fraction of unreacted Mg, while a fraction of very weak peaks could not be indexed and were ascribed to the presence of impurities.

Preliminary structural analysis with the Simulated Annealing algorithm allowed us to identify a reliable starting model for the Rietveld refinement, which is however still in progress. In such structure, C_{60} molecules are arranged in a hexagonal close packed lattice, while THF molecules are coordinated to Mg^{2+} ions, forming columns with a three-fold symmetry (see Figure 3). A rough estimation of the amount of unreacted Mg, compared with the nominal stoichiometry of 5 Mg atoms per C_{60} introduced during the synthesis, allowed us to assume the formula $MgC_{60}(THF)_3$ for this crystalline compound. The presence of pure Mg in this sample prevented us to thorough study the transport properties of this compound so far, but we expect that, due to the strong increase of the cell volume (the volume per C_{60} molecule changes from ~710 Å^3 in pure C_{60} to ~994 Å^3), the compound could have an insulating behaviour.
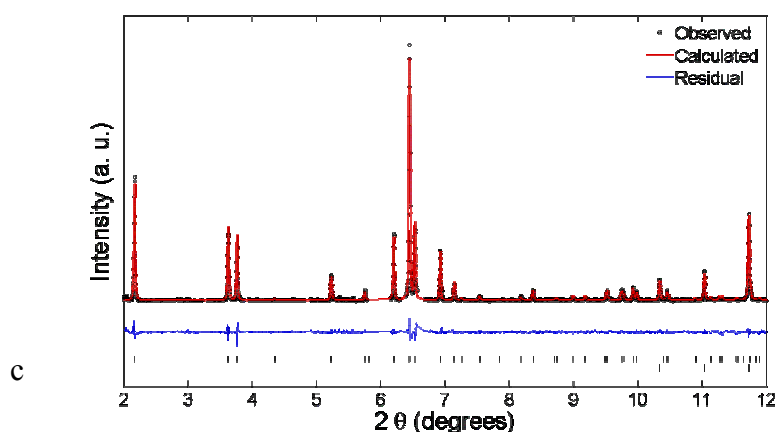
Thermal evolution of the lattice parameters on cooling the sample down to 10 K did not show the presence of any evident structural phase transition, while the estimated thermal expansion coefficients roughly resembles those of monomer phases of intercalated C_{60} compounds ($\alpha_a = 3.8 \cdot 10^{-5}$ K^{-1}, $\alpha_c = 7.8 \cdot 10^{-5}$ K^{-1}).
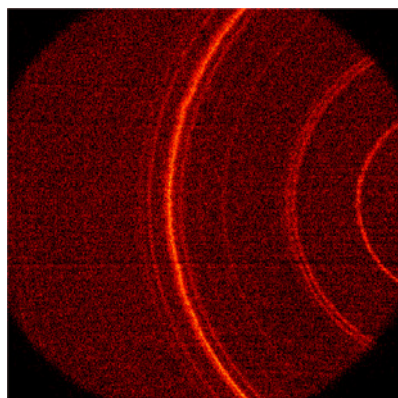
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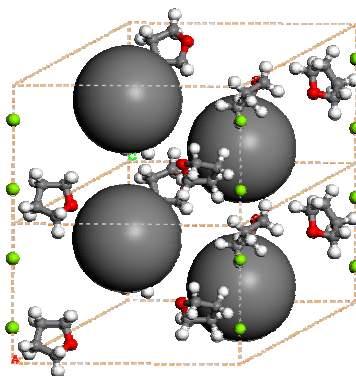
b

c

Figure 1: a) 2D powder diffraction image collected on 1 mm diameter capillaries of $MgC_{60}(THF)_3$ (Bruker D8 Discover with GADDS, copper anode). b) Proposed structure of $MgC_{60}(THF)_3$. c) Comparison of calculated and symulated powder diffraction pattern of $MgC_{60}(THF)_3$ (Le Bail analysis, $R_{wp} = 9.32\%$), The stronger peaks at higher 2θ angle are due to the presence of unreacted Mg.

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. mazzani, M. Riccò, I. Margiolaki and D. Cheptiakov, J. Am. Chem. Soc., manuscript in preparation.