

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.

Published papers

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.



	Experiment title: Structural transitions in mixed alkali intercalated fullerides: from Li ₄ C ₆₀ to Na ₄ C ₆₀	Experiment number: CH-1888
Beamline: ID31	Date of experiment: from: 22.04.2005 to: 26.04.2005	Date of report: 06.02.2006 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Dr. Irene MARGIOLAKI	
Names and affiliations of applicants (* indicates experimentalists): Dr Toni SHIROKA* Dr Serena MARGADONNA* Mr Daniele PONTIROLI* Dr Mauro RICCÒ*		

Report:

Under extreme conditions (high pressure and high temperature) pure fullerene C_{60} , can easily polymerise by establishing covalent bonds between its molecular units [1]. The same effect is obtained also by the intercalation of alkali atoms in the lattice interstices of the host fullerene structure. In this case, if the cation hindrance does not interfere with the closer polymer packing [2, 3], the charge transfer from alkali to the buckyballs will provide the necessary “chemical pressure”. In particular, small-alkali doped fullerenes have shown an unexpected wealth of polymerised structures, characterised by the presence of four membered carbon rings ([2+2] cycloaddition reaction), by single C-C bonds, or even by a combination of the former bonding motifs, as in Li_4C_{60} [4, 5].

To gain a better insight into the unusual polymeric structure of Li_4C_{60} , part of the allocated beam time was dedicated to the detailed study of its thermally induced polymer-to-monomer transition. As already found in a previous work [see report 2004 CH-1629], a moderate heat treatment leads to the disruption of the Li_4C_{60} polymer and to the simultaneous formation of a *fcc* monomer phase, a process which completes at $\sim 350^\circ\text{C}$. Here we investigated the thermal evolution of the monoclinic (polymer) and cubic (monomer) cell parameters in the temperature range $25\text{--}450^\circ\text{C}$. A two-phase Le Bail pattern decomposition allowed the extraction of cell parameters, whose temperature dependence is shown in Fig. 1. In both cases the thermal expansion was almost constant in the explored temperature range, hence a linear fit could give the following thermal coefficients: $\alpha_a = 4.4(2) \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_b = 1.7(3) \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_c = 22(1) \cdot 10^{-6} \text{ K}^{-1}$ and $\alpha_{a\text{-}cub} = 9(1) \cdot 10^{-6} \text{ K}^{-1}$. Focussing on the *a* and *b* cell edges, along which the polymerisation takes place, we notice a much smaller thermal expansion (by an order of magnitude) with respect to that along the stacking direction *c* or a_{cub} . On the other hand, the latter values are fully compatible with those obtained in other monomer C_{60} compounds [6]. The ratio $\alpha_a \cdot \alpha_b$, approximately 2:1, fully confirms the hybrid nature of the polymer. Moreover, no extra phases were observed in the powder diffractograms collected during the polymer-to-

monomer transition. The absence of intermediate structures or steep variations in thermal coefficients suggests the simultaneous breaking of both C-C bridging motifs, despite their different bonding nature.

The rest of the beam time was devoted to the structural investigation of $\text{Li}_x\text{Na}_{4-x}\text{C}_{60}$ series ($0 < x \leq 4$), both at room and at high temperatures. Since Na_4C_{60} is an already well known 2D single-bonded polymer [3], our comparative study can evidence possible new, hybrid polymer phases, thus allowing a deeper understanding of the carbon polymerisation mechanism.

Room temperature diffraction shows the segregation of two polymer phases, respectively Li_4C_{60} and Na_4C_{60} , as lithium is progressively substituted by sodium. Surprisingly, the $x = 3$ phase shows the same structure as Li_4C_{60} , suggesting the stability of this mixed structure. A totally different scenario opens up at high-temperatures (see Fig. 2), where a wealth of different monomer phases was observed. In fact, the $x = 3$ compound presents a similar cubic *fcc* arrangement as that of $x = 4$. Monomer Na_4C_{60} , on the contrary, shows a tetragonal structure, with a minority cubic phase, as already observed in a previous work [7]. Finally, in the intermediate doping range ($x = 2, 3$), an unusual hexagonal close packing of the buckyballs is observed. Focussing in particular on $\text{Li}_2\text{Na}_2\text{C}_{60}$, representative of this class, the powder pattern could be indexed as *P* $63/m\ m\ c$, $a = 10.0726(2)$, $c = 16.5570(5)$ ($R_{wp} = 5.44\%$, Le Bail analysis). Moreover, the collected data indicate typical distortions due to stacking fault defects, as evinced by the non homogeneous broadening of the peaks satisfying the condition $h - k = 3t \pm 1$ ($t = \text{integer}$) [9]. Detailed analyses are still in progress.

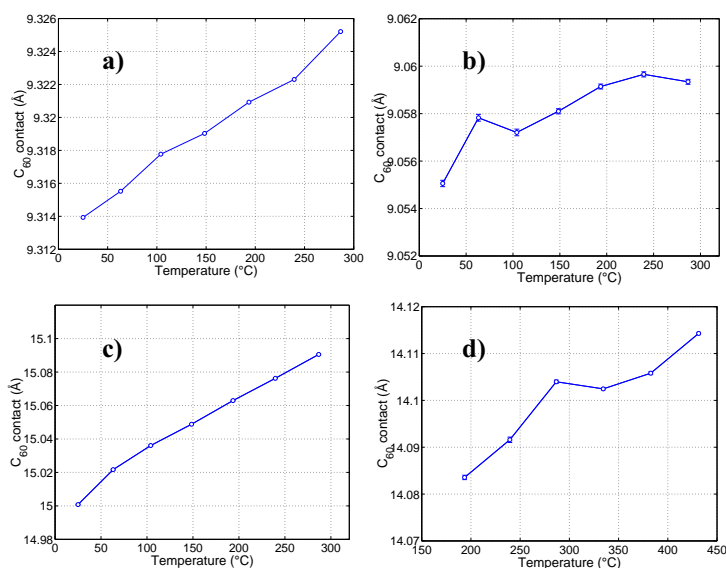


Fig. 1: Temperature evolution of the monoclinic (a-c) and cubic (d) cell parameters in Li_4C_{60} .

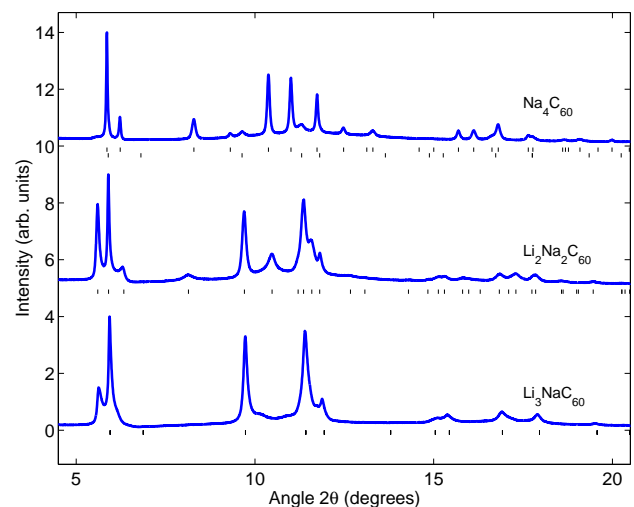


Fig. 2: High resolution powder diffraction patterns of $\text{Li}_x\text{Na}_{4-x}\text{C}_{60}$ monomer phases. The ticks mark the reflection positions.

References

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