	Experiment title: Study of the Structural Phase Diagram of the Intercalated Fullerides Li_xC_{60} ($4 < x < 6$)	Experiment number: CH-1629
Beamline: ID31	Date of experiment: from: 31.10.2003 to: 03.11.2003	Date of report: 20.04.2004
Shifts: 9	Local contact(s): Dr. Michela Brunelli	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Toni SHIROKA* - Dipartimento di Fisica, Università di Parma, ITALY Dr. Daniele PONTIROLI* - Dipartimento di Fisica, Università di Parma, ITALY Dr. Serena MARGADONNA* - Chemistry Department, Cambridge University, UK		

Report:

It is already well known that fullerene-based compounds, under particular conditions (pressure, heating, doping, etc.), can form different types of polymeric structures [1]. The study of doping-induced polymerisation is particularly interesting as, when compared with the other types of polymerisation, it would allow a better insight into the mechanisms which determine the bonding among the C_{60} molecules. Among the alkali-intercalated fullerides with stoichiometries A_xC_{60} , those involving lithium are somewhat particular due to the rather small radius and the weak electropositivity of Li^+ ions, which enhances the tendency to form polymerised structures.

Li_4C_{60} was chosen for detailed structural analysis as a function of temperature in an effort to determine the structures of the polymeric phases and to systematically study the fullerene polymerisation/depolymerisation reaction. Moreover, room temperature (RT) measurements were performed in the whole Li_xC_{60} series with stoichiometries $x = 3, 3.5, 4, 4.5, 5$.

We focused our efforts on the Li_4C_{60} α -phase (as prepared), which is different from that obtained after a thermal cycle up to $\sim 400^\circ\text{C}$ and back to RT.

The results of high-resolution diffraction measurements on heating the Li_4C_{60} sample are shown in fig. 1. The rich diffraction pattern at room temperature, arising from the presence of fullerene polymerisation which lowers the overall symmetry, is progressively simplified as the temperature rises. Especially significant is the behaviour of the first peak (at $2\theta \sim 6^\circ$) which goes from a superimposition of three distinct reflections at room temperature to a single, well-defined peak at 350°C . Similar structural reorganization towards a higher symmetry is observed also from the disappearance of the peaks occurring respectively at 7.48° , 10.44° , 12.32° and 19.29° , as shown by arrows in fig. 1.

We first indexed the high resolution diffraction profile of Li_4C_{60} collected at room temperature (fig. 2). The most obvious choice was to start from a structure with pseudo-tetragonal symmetry, as suggested from recent

works on similar compounds [2, 3]. However the overall agreement was unsatisfactory, as reflections in the 2θ region $10 \div 11^\circ$ were not accounted for. By lowering the symmetry of the structure from $I m m m$ to $I 1 2/m 1$, it was possible to fit all the peaks of the pattern. A successive Le Bail analysis [4] using the Fullprof program [5] confirmed that Li_4C_{60} adopts a monoclinic structure with lattice constants of $a = 9.32 \text{ \AA}$, $b = 9.05 \text{ \AA}$, $c = 15.03 \text{ \AA}$ and $\beta = 90.96^\circ$ in the space group $I 2/m$ ($R_{\text{wp}}=4.88\%$, $R_p=3.52\%$). Along the b -axis the interfullerene separation is of 9.05 \AA and this is a clear evidence of the presence of polymeric chains, where the C_{60} units are joined by 2 single C-C bonds, formed via a 2+2 cycloaddition reaction (fig. 3). However, along the a -axis, the buckyballs distance is of 9.32 \AA , which is an indication that in that direction the C_{60} units are linked by a single C-C bond. This leads to the formation of a novel 2D polymeric network with different types of bonding along the two axes.

Currently NMR MAS measurements are being performed in which, by evaluating the intensity ratio I_{sp^3}/I_{sp^2} for the NMR signal from sp^3 and sp^2 carbon atoms, we will detect the total number of bonds [6] and thus verify the existence of a 2D polymer.

Rietveld refinements to determine the effective lithium positions in the lattice are still in progress. Locating the alkali atom inside the lattice is quite difficult, since it scatters x-rays very weakly and is extremely mobile (from NMR data the lithium blocking temperature seems to be below 5 K).

From an analysis of the RT patterns for different lithium stoichiometries ($x = 3, 3.5, 4.5, 5$) we find that the crystal structure remains substantially unchanged. Nevertheless, there is a clear evidence of a reduction of monoclinic distortion with the increase of lithium doping.

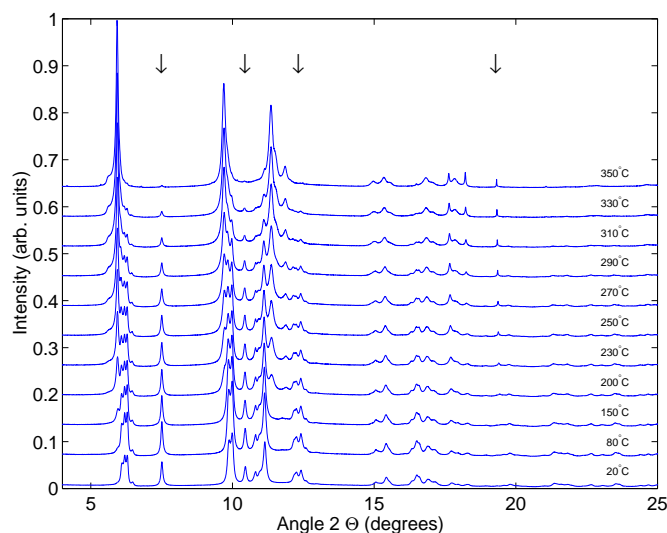


Fig. 1: Temperature evolution of the Li_4C_{60} diffraction patterns on heating. Notice the structural modifications shown by arrows.

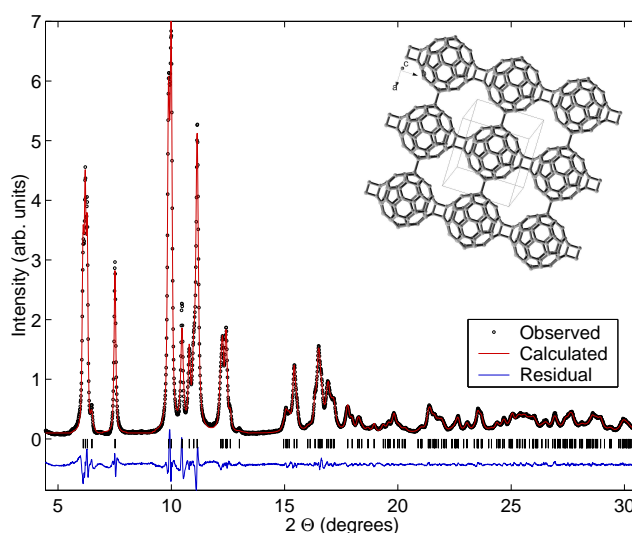


Fig. 2: Measured (o) and calculated (solid line) diffraction pattern of Li_4C_{60} at 300 K (α -phase). The lower solid line shows the difference profile and the tick marks the reflection positions. Inset: the polymeric structure of Li_4C_{60} (α -phase).

References

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