

## 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:**

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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.

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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.



	<b>Experiment title:</b> Structural investigation of hole doped fullerenes	<b>Experiment number:</b> CH-2387
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 20.04.2007 to: 23.04.2007	<b>Date of report:</b> 09.06.2008
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Michela Brunelli	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Dr Daniele PONTIROLI*</b> <b>Dr Mauro RICCÒ*</b> <b>Mr Fabio GIANFERRARI*</b>		

## Report:

“*Hole doped*” fullerene based compounds are very interesting systems, which however received very exiguous attention until now [1, 2], especially because of the difficulties which one encounters during their preparation. In fact, the relatively high oxidation potential of  $C_{60}$  [3] and its tendency to undergo nucleophilic attack from the most common oxidant chemical species, put stringent limits to the choice of the suitable counter-ion in an hypothetical fullerenium salt. The interest in this class of compounds is mainly due to their expected noticeable high  $T_c$  in case that a superconducting “*hole doped*” phase was prepared. This behaviour is clearly predicted by either the standard BCS Theory (in the Migdal Eliashberg extension) or even by the still debated more recent non-adiabatic theories of superconductivity [4], which proved to describe quite well the already known “*anionic*” superconducting fullerenes [5].

In this report we discuss the results of the analysis of high resolution powder diffraction data collected on the fullerenium salt  $C_{60}(AsF_6)_2$  at ID31, in which  $C_{60}$  is found in the charged state  $C_{60}^{2+}$ . To our knowledge, this is the first time that a stable compound in which  $C_{60}$  is in the oxidised state and with a good crystal quality is prepared and undergoes a detailed structural study.

Our results shows that the species  $C_{60}^{2+}$  in the solid state is extremely reactive and stabilises by promoting an unusual *1D zigzag polymer*. This unique ground state prevents the compound to display any metallic behaviour and hence any superconducting transition.

Data were collected at room temperature ( $\lambda = 0.9337 \text{ \AA}$ ) in the Debye Scherrer geometry; the sample was sealed in a quartz capillary of 0.5 mm diameter. The diffraction pattern shows slightly broad and asymmetric peaks with strongly Lorentzian shape; because of the extremely narrow instrumental response, the main contribution to the broadening could be ascribed to the size and strain effects arising from the sample. Almost all the peaks of the pattern were easily indexed with an orthorhombic cell, while the systematic extinctions were observed accordingly to the spatial group *Imma*. If one admits that, in absence of strong

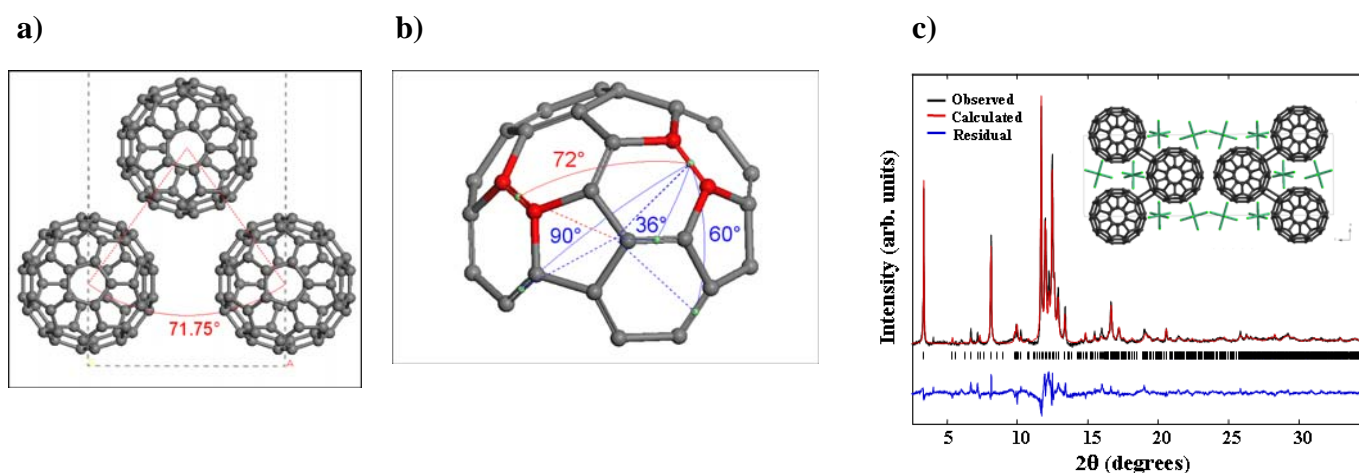
intra-molecular interactions both  $C_{60}$  and the  $AsF_6^-$  anions should pack as spheres, the observed symmetry looks somewhat strange and requires a non trivial cell transformation to be explained. Hence, this distortion is a hint of a more complicated molecular arrangement.

The coarse disposition of the molecules into the asymmetric unit was obtained with the use of the *simulated annealing* algorithm; the choice of the number of molecules inside the cell were constrained by the knowledge of the compound density,  $\sim 2.2 \text{ gr/cm}^3$ , and of the stoichiometry ratio 1:2 between  $C_{60}$  and  $AsF_6^-$ , provided by elemental analysis (ICP – OES). A good agreement with the data was obtained by sitting the centres of mass of both the two molecular species into the special positions  $4e$  (0,  $\frac{1}{4}$ ,  $z$ ), with respectively  $z=0.86$  for  $C_{60}$ ,  $z=0.69$  and  $z=0.55$  for the two  $AsF_6^-$  ions.

At this step, we noted that  $C_{60}$  units were placed very close, with a closest contact of  $\sim 9 \text{ \AA}$ , thus suggesting that fullerenes should be bonded. If compared with the alkali doped polymers, the intermolecular distance is compatible with a link by [2+2] cycloaddition reaction. This connection is established along directions which form an unusual *zigzag path* with an angle of  $\sim 72^\circ$ , as shown in Fig. 1a). A strong confirmation of such polymerisation was provided by a more careful analysis of the disposition of *single bonds* (namely the bonds shared by two hexagons) on the fullerene cage (Fig. 1b)). In fact, these bonds on the non-distorted buckyball are observed in positions which form angles of  $36^\circ$ ,  $60^\circ$ ,  $90^\circ$  and even  $72^\circ$  degrees. One could easily recognise that the bonds at  $90^\circ$  are involved in the tetragonal polymers, while those at  $60^\circ$  recur in the rhombohedral polymer. Polymers with bonds forming 36 and 60 degrees have been never observed because of obvious limitations due to the sterical hindrance of the fullerene itself, but an arrangement with fullerenes at  $72^\circ$  is in principle allowed and it is just what we observe in our compound.

As far as the  $AsF_6^-$  ions are concerned, they actually occupy the voids among the carbon backbone and their position is disordered around the special position  $4e$ . Even if the refined thermal factors are high, these molecules cannot rotate freely around their centre of gravity, due to sterical constrictions, but rather they librate around their equilibrium positions.

The result of the Rietveld refinement ( $R_{wp}$  4.33%,  $R_{exp}$  1.16%) is shown in Fig. 1c), while the crystal structure is displayed in the inset.



**Fig 1:** **a)** Disposition of the  $C_{60}$  molecules into the orthorhombic cell of  $C_{60}(AsF_6)_2$ . **b)** The angles formed by “double bonds” on the fullerene molecule. **c)** Observed (in black) and calculated (in red) diffraction profile of  $C_{60}(AsF_6)_2$  at 300K ( $R_{wp}$  4.33%,  $R_{exp}$  1.16%). *Inset:* crystal structure of  $C_{60}(AsF_6)_2$  polymer.

## References

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3. C. Bruno et al., *J. Am.Chem. Soc.* **125**, 15738 (2003).
4. E. Cappelluti, C. Grimaldi, L. Pietronero and S. Strässler, *J. Mod. Phys. B* **14**, 2950 (2000) ; P.Paci, E. Cappelluti, C. Grimaldi, L. Pietronero S, Strassler, *Physica C* **408-410**, 240 (2004).
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