



	Experiment title: Structural study of $\text{Li}_{12}\text{C}_{60}$.	Experiment number: CH-333
Beamline: BM16	Date of Experiment: from: 23-Oct-97 to: 30-Oct-97	Date of Report: 29-Jul-98
Shifts: 9	Local contact(s) : A.N. Fitch, E. Dooryhee	Received at ESRF: 08 SEP. 1998

Names and affiliations of applicants (*indicates experimentalists):

Luigi Cristofolini,
Mauro Riccò
Dipartimento di Fisica,
Università degli Studi di Parma,
via delle Scienze,
I-43100 Parma, Italy

Report:

The intercalation of large radius alkali metals in the fullerene pristine structure is well known to yield salts of stoichiometry A_xC_{60} ($x=1,3,4,6$; $\text{A}=\text{K}, \text{Rb}, \text{Cs}$) which may support superconductivity (as in the case of A_3C_{60}) and magnetism (as in the case of A_1C_{60}). A natural limit in the doping level is reached at $x=6$ due to the complete occupancy of the voids of the pristine cubic structure. On the contrary, smaller radius Li and Na (ionic radii = 0.63, 0.97 Å respectively) may yield phases with higher alkali metal content, either due to the tendency to form metallic clusters located in the voids of the pseudo cubic fullerene structure, as is the case of $\text{Na}_{11}\text{C}_{60}[1]$, or possibly to form alkali metal- fulleroid super clusters [2]. We have studied the structure of different Lithium doped fulleride Li_xC_{60} compounds at different temperatures ranging from 90K to 553K. The results can be summarized as follows:

- The stoichiometry $x=12$ represents the minimum Li doping for a phase whose structure is strikingly similar to that of pristine C_{60} and which extends to much larger Li doping levels x .
- $\text{Li}_{12}\text{C}_{60}$ is face centered cubic *fcc* at high temperature (553K), in analogy with pristine C_{60} ; we were able to perform a Rietveld refinement of its structure.
- The structure of $\text{Li}_{12}\text{C}_{60}$ distorts from *fcc* to *bct* tetragonal upon cooling.

The temperature dependence of the lattice parameters extracted by the Le Bail technique is shown in figure 1 for both the *bct* and the *fcc* phases.

In figure 2 we report the diffraction pattern collected on $\text{Li}_{12}\text{C}_{60}$ at $T=553\text{ K}$ ($\lambda = 0.652924\text{ \AA}$) together with its Rietveld refinement ($R_{wp}=10.9\%$, $R_I=6.9\%$, $R_{exp}=2.5\%$) obtained in $Fm\bar{3}m$ symmetry, with the C_{60} units modeled as symmetry adapted spherical harmonic functions (SASH) [3, 4] centered in 4a (0,0,0). The resulting density of carbon on the C_{60} sphere is maximum in the lattice directions (1,0,0) and $(\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$, while it is minimum in the (1,1,1) direction which points towards the tetrahedral void.

In comparison in $\text{Li}_2\text{CsC}_{60}$ [5] a negative value found for $C_{10,1}$ implies an excess of carbon density in the (1,1) direction which corresponds to Li ions residing in the tetrahedral void. The Li ions are localized in a cluster located at the octahedral void, while the tetrahedral void 8c refines to zero Li occupancy. In conclusion, $\text{Li}_{12}\text{C}_{60}$ has cubic symmetry at 553K and distorts to tetragonal upon cooling. The high T structure of $\text{Li}_{12}\text{C}_{60}$ is that of an intercalation compound with all the Li ions concentrated in the octahedral voids, with strong indications of co-ordination between Li ions and the carbon density on the nearest C_{60} unit.

References

- [1] T. Yildirim et al., Nature 360, 568 (1992)
- [2] J. Kohanoff et al., Chem Phys Lett 198, 472 (1992)
- [3] W. Press A. Huller, Acta Crystallographica A, 29 , 252 (1973) J. P. Amoreaux, M. Bee, Acta Crystallographica B, 36, 2636 (1980), J.K. Cockroft A. Fitch, Z. Kristallogr 184, 123 (1988).
- [4] L. Cristofolini, M. Riccb, R. De Renzi, in preparation
- [5] I. Hiroswawa et al., Science 264, 1294 (1994)

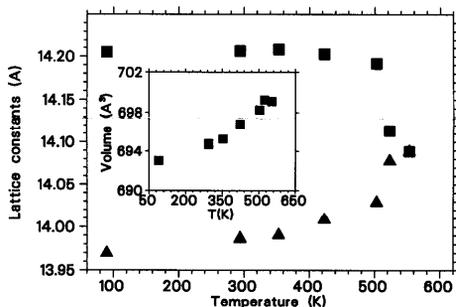


Fig 1: Temperature dependences of the lattice parameters c (squares) and a (triangles, scaled by $\sqrt{2}$) from BM16 data on $\text{Li}_{12}\text{C}_{60}$. **Inset:** volume per C_{60} unit (in Å^3).

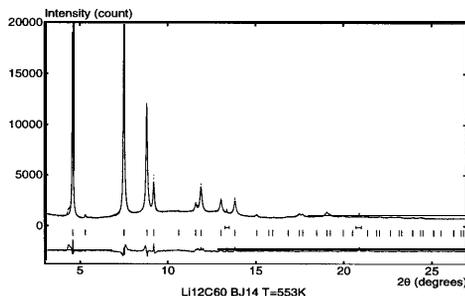


Fig 2: Diffraction pattern collected on BM16 (dots) and its Rietveld refinement (line). The 28 regions 13.25° - 13.50° and 20.70° - 21.00° have been excluded from the fit.