ESRF	**Experiment title:** In situ diffraction study of C60 phase diagram using LV cell coupled with the fast scan 2D detector	**Experiment number:** HS 752
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Report:

Fullerene molecules, as other non-saturated systems, have been shown to polymerize either photochemically or under high pressure and high temperature (HP-HT). HP-HT methods, in opposite to photochemical method, yield C60 structures consisting of ordered arrays of polymerized C60 molecules. X-ray diffraction studies have shown that these polymeric structures are, depending on the pressure-temperature conditions of preparation, either one-dimensional (1D), two-dimensional (2D) or three dimensional (3D), implying a polymerization reaction that proceeds along some preferred directions and not at random.

In the 1D polymer, the C60 molecules are linked into polymeric chains while in the 2D polymers they form hexagonal or square polymerized layers. In the 3D polymer the molecular bonding occurs in the 12 first neighbor directions. Synchrotron radiation powder diffraction measurements using a fast image plate detector was firstly performed on quenched 3D C60 polymerized samples. Structural analysis of diffraction patterns have shown that this 3D polymer exhibits unusual ellipsoidal Debye-Sherrer diffraction patterns. 1D diffraction profiles taken on arbitrary azimuthal directions of these spectra can be

perfectly indexed on a fcc fullerite compressed whose cell parameter varies continuously with the angle of azimuth.

This effect has been extensively studied in situ at high pressure and high temperature in the Paris-Edinburgh set up of ID30 beamline. The in situ diffraction patterns exhibits the same elliptical shape as that of the quenched 3D polymer. The continuous loci of the Bragg reflections are elliptical and not circular, as expected for normal powder Debye-Sherrer patterns obtained with a 2D detector placed perpendicular to the beam axis. These ellipsoidal patterns are due to the deviatoric stress that results from the uniaxial character of the force that is used to establish the pressure. The elliptical shape results from a larger compressions of the cristallographic lattice parameters in the direction of the applied force, as the magnitude of each inter-planar distance d_{hkl} is a function of its orientation with respect to the stress field within the sample. The ellipsity could be huge (up to 9%) and could be retained in quenched samples. As the compressed polymerized fullerite samples have been produced in non-hydrostatic conditions, we must conclude that the intermolecular bonding is capable of freezing the stress gradient under which these phases are prepared. The orientation of the uniaxial stress is unique in the bulk sample and, depending to its orientation relatively to the x-ray beam, different anisotropic patterns are observed.

One can add that the systematic in situ investigation of the P-T phase diagram of C60 in the Paris-Edinburgh press has shown a much more complex beahaviour than previously admitted. Indeed, depending on the P-T path and not only on the P-T values of the synthesis the phase transformations can be significantly different. For instance, when the polymerization initiates in the orientationally ordered state, ordered structures of C60 are formed. While, when the polymerization initiates in the orientational disordered state, the polymerization takes place at random and an isotropic polymer is formed, giving rise to fcc patterns as it is for photo-polymerized fullerites.

More details concerning this work can be found:

L.Marques et al. Science 283, 1720 (1999).

M.Mezouar et al. (to appear in ESRF newsletter)