

"DEBYE-SCHERRER ELLIPSES": A GIANT ANISOTROPIC DEFORMATION IN C_{60} POLYMERS AT HIGH PRESSURE AND HIGH TEMPERATURE

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"Debye-Scherrer Ellipses" provide evidence of a giant anisotropic deformation in C_{60} polymers, produced under elevated temperature and pressure conditions, which may be retained at ambient pressures.

Since C_{60} became available to researchers in the solid state and in suitable quantities, there have been predictions of possible interconnected fullerene lattices with interesting properties. Such phases would result in denser and more saturated species having a more pronounced sp^3 character and they would allow the building of new host structures, based only on a pure carbon framework. High pressure studies have determined the existence of 1-D and 2-D polymer structures, made up of C_{60} molecules attached through 2+2 cycloaddition bonds. More recent x-ray synchrotron radiation measurements performed at the ESRF have demonstrated the existence of a 3-D arrangement of polymerized fullerene molecules. Ellipsoidal x-ray Debye-Scherrer diffraction patterns, the signature of a giant anisotropic deformation, have been observed during *in situ* and quenched experiments at high pressure and high temperature. This unusual effect, related to the process of deformation of the C_{60} cages during the compression, is retained at ambient pressure by 3-D intermolecular bonding or released in the case of low-dimensional polymers.

POLYMERIC STRUCTURES

Fullerene molecules, like other non-saturated systems, have been shown to polymerize either photochemically or under high pressure and high temperature (HP-HT) [1-2]. Molecular rotation is needed for the photopolymerization to be accomplished, and it probably occurs at random. Little is

known about the photopolymer structure because its x-ray diffraction pattern presents broad peaks centered at fcc lattice positions, corresponding to a slightly contracted cell in comparison with the monomer cell. Conversely, high pressure and high temperature (HP-HT) yields C_{60} structures consisting of ordered arrays of polymerized C_{60} molecules. X-ray diffraction studies have shown that these polymeric structures are, depending on the pressure-temperature conditions of preparation, either one-dimensional (1-D), two-dimensional (2-D) or three-dimensional (3-D) implying a polymerization reaction that proceeds along some preferred directions and not at random.

In the 1-D polymer, the C_{60} molecules are linked into polymeric chains while in the 2-D polymers they form hexagonal or square polymerized layers (Figure 1). In the 3-D polymer, the molecular bonding occurs in the twelve nearest neighbor directions. Synchrotron radiation powder diffraction using a fast image plate detector was first performed on quenched 3-D C_{60} polymerized samples. Structural analysis of diffraction patterns have shown that this 3-D polymer exhibits unusual ellipsoidal Debye-Scherrer diffraction patterns [3]. This unusual effect is illustrated in Figure 2. 1-D diffraction profiles taken on an arbitrary azimuthal direction of these spectra can be perfectly indexed on a fcc fullerite compressed lattice whose cell parameter varies continuously with the angle of azimuth.

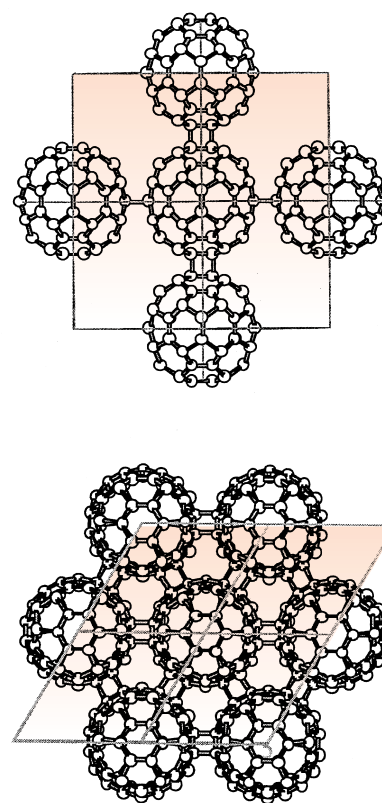


Fig. 1: Examples of (2+2) intermolecular bonding occurring in 2-D fullerite polymers.

IN SITU ANALYSIS

This effect has been extensively studied *in situ* at high pressure and high temperature in the Paris-Edinburgh setup of ID30 (Figure 3) which has previously been described in detail [4]. A typical diffraction pattern obtained at $P = 2$ GPa and $T = 473$ K using this setup is presented in Figure 4. It was evident that the *in situ* diffraction pattern exhibits the

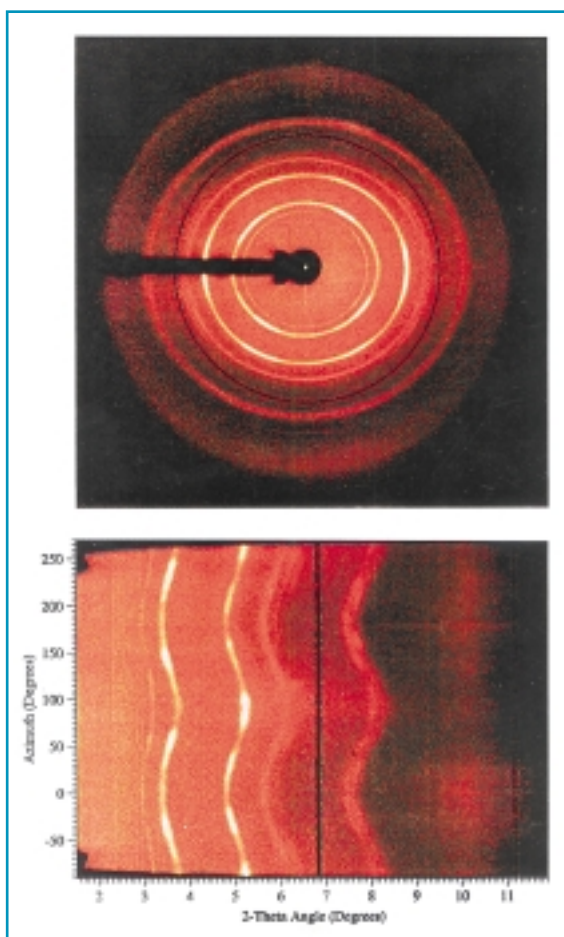


Fig. 2: Diffraction image and the corresponding unrolled projection along an azimuthal angle (an entire ring corresponds to 360° variation of the azimuthal angle) of the 3-D C₆₀ polymer (from [3]).

same elliptical shape as that of the quenched 3-D polymer. The continuous loci of the Bragg reflections in Figure 4 are elliptical and not circular, as expected for normal powder Debye-Scherrer patterns obtained with a 2-D 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 was used to establish the pressure. The elliptical shape results from a larger compression of the crystallographic lattice parameters in the direction of the applied force, as the magnitude of each inter-reticular distance d_{hkl} is a function of its orientation with respect to the stress field within the sample. On

compounds other than fullerenes, such an effect is much smaller (ellipsity < 1%) and is only observed *in situ* at high pressure.

A HUGE ELLIPSITY

In contrast, the fullerene ellipsity can be huge (up to 9%) and retained in quenched samples. As the compressed polymerized fullerite samples have been produced in non-hydrostatic conditions, we must conclude that the inter-molecular 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 on its orientation relative to that of 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-Edinburg press has shown a much more complex behavior 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 orientationally 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 fullerenes.

This study demonstrates the ability of the large volume press in the *in situ*

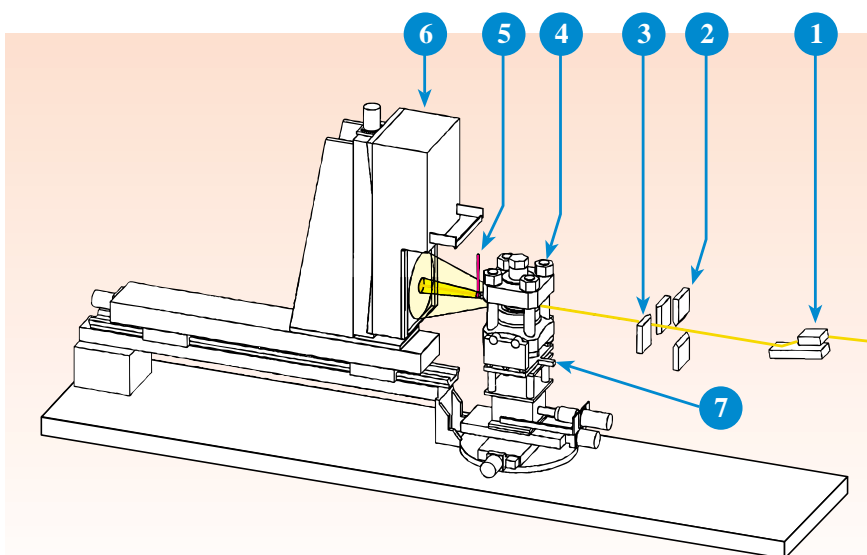


Fig. 3: Layout of the High Pressure beamline ID30 at the ESRF in large-volume press configuration. 1: Si(111) channel-cut monochromator, 2-3: Tungsten carbide slits, horizontal and vertical limits, 4: Paris-Edinburgh large-volume press, 5: Beam stop, 6: Fast-scan, 7: Press holder.



synchrotron diffraction studies for low-Z elements. Depending on the p-T path used for the synthesis of fullerite polymers, a continuous range of phase transformations can be reached, from disordered to ordered phases and from 1-D to 3-D phases. This latter phase is likely to be a continuous network of mainly sp³ carbon atoms with large cages placed periodically, that is a carbon zeolite. Furthermore the Debye-Scherrer "ellipses" and the large anisotropic deformation observed on C₆₀ indicate that this material can support, visualize and memorize large uniaxial stresses. ■

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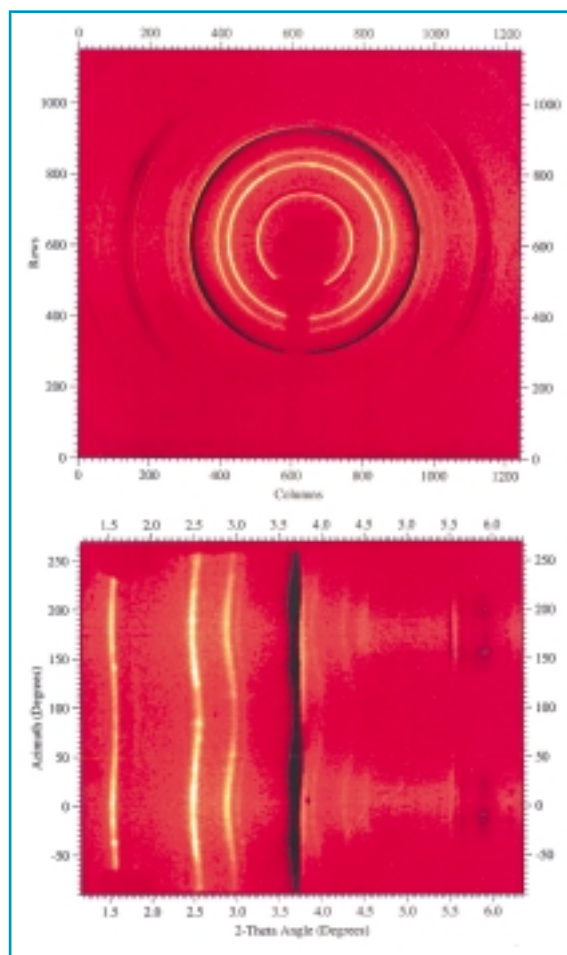


Fig. 4: In situ diffraction image and the corresponding unrolled projection along an azimuthal angle. The pressure and temperature of the experiment were $P = 2$ GPa and $T = 473$ K.

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