*In situ* x-ray diffraction studies of three-dimensional C$_{60}$ polymers

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## Abstract

*In situ* investigations into the $P/T$ field of C$_{60}$ fullerene were performed using energy-dispersive x-ray diffraction techniques. Isobars were obtained at 11 and 9 GPa accompanied by isotherms at 750 and 800 K with pressure reaching 13 GPa. The $P/T$ history and pressure isotropy were investigated with the aim of optimizing conditions for 3D polymer formation. Confirmation of the formation of 3D polymers was performed *in situ*; however, the reclaimed sample did not exhibit the expected high hardness value, due to depolymerization on pressure release. Isotropy in the pressure field promoted formation and retention of the face-centred-cubic structure.

## 1. Introduction

In the mid-1980s a new allotrope of carbon was discovered by Kroto *et al* [1]. The discovery of a facile synthesis route by Kratschmer *et al* [2] generated huge interest in the science community resulting in the discovery of 1D and 2D polymers as photo-transformed thin films [3]. The intermolecular connections are four-membered, sp$^3$ covalently bonded rings formed by the [2 + 2] cycloaddition of two adjacent '66' bonds [4]. High-pressure and high-temperature treatments permitted the formation, in bulk quantities, of a whole new range of carbon states [5–8]. At moderate pressures and temperatures 1D orthorhombic, 2D tetragonal and rhombohedral polymers form [7–10] and the latter has recently been shown to exhibit ferromagnetic properties [11], due to the formation of unpaired radical bonds prior to graphitization. However, with more extreme conditions, cage collapse is total, forming graphitic 'hard' carbons, which are predominantly sp$^2$ in character [12, 13].

Overall, the reaction diagram [14, 15] is well known and agreed, with discrepancies due to variations in the shear and pressure uniaxiality of the apparatus. To investigate this and cover the rest of the $P/T$ field, we have extended the previously reported *in situ* x-ray studies [16],

with special emphasis on the formation of 3D polymers [17–19], to ultrahigh pressures, using variations in the $P/T$ history to optimize synthesis.

## 2. Experimental details

The *in situ* diffraction spectra were taken at the Spring-8 high-powered (8 GeV) x-ray synchrotron in Japan. The High Temperature Research BL04B1 beamline utilizes a SPEED 1500 high-pressure isostatic press with tungsten carbide anvils, which gave access to pressures up to 13 GPa. A gap of $0.05 \times 0.2$ mm in the anvils allows a beam of white x-rays access to the sample; these are then collected using an energy-dispersive solid-state germanium detector at a $2\theta$ angle of $3.5°$. The $C_{60}$ was obtained as a 99.9% purity powder from the Materials and Electrochemical Research (MER) Corporation. The pressure-transmitting media were MgO powder for generating a quasi-hydrostatic field and solid $Al_2O_3$ discs to produce anisotropy in the pressure field.

Five runs were completed in the experiment. Two isobars were completed at 11.1 GPa, with varying pressure isotropies, to a temperature of 750 K and then quenched at a rate of 30 K s$^{-1}$. A third isobar was taken at 9 GPa to fill gaps missed in the $P/T$ range during previous experiments [16]; the isobaric runs increased in temperature with 50 K increments and were held for 400 s—the acquisition time of the XRD spectra. An isotherm at 800 K and a history-dependent run made up the final two experiments; these two runs had reduced holding times of 200 s, which did not affect the quality of the traces.

The hardness values acquired were averages of ten separate micro-indents from various areas of each sample. The load applied varied from 250 mN for the soft samples up to 1000 mN for the graphitic 'hard' carbon. The Raman spectrum for run 4 was taken on a Dilor Modular XY Raman Spectrometer which uses a 5 W argon-ion laser.

## 3. Results and discussion

The first run was performed along the 11.1 GPa isobar; the evolution of this XRD trace is displayed in figure 1. The room temperature and pressure trace is as expected, with familiar strong (111), (220) and (311) FCC peaks at about 8, 5 and 4.5 Å respectively. For simplicity, the original cubic index system is used to describe the spectral evolution. The application of pressure on the sample will affect the unit-cell volume, and hence reduce the $d$-values of the peaks still visible. The shifting of the (220) peak from approximately 5 to 4.5 Å indicates the magnitude of this contraction, which corresponds to a reduction in unit-cell parameter from 14.16 to 12.61 Å. This phenomenon will occur whenever pressure is applied and, conversely, when it is removed; thus care must be taken not to mistake it for a 'real' change in the unit-cell parameters due to polymerization. The application of pressure, and a little increase in temperature, also resulted in a change in peak intensities. The most noticeable case of this involves the near disappearance of the strong (111) peak accompanied by the appearance of the originally absent (200). The changes in these peaks are related to the molecular form factor, which influences the diffraction selection rules, of the $C_{60}$ molecule. In this case it is simply an indication of how distorted the molecule has become from its original sphere. The main cause of distortion to the molecule would be intermolecular bonding. This would distend the $C_{60}$ sphere in the direction of bridge bond formation. It is therefore evident that dimerization and polymerization are commencing at temperatures between 300 and 350 K. The minimal amount of heat required to initiate polymerization indicates that the polymerization mechanism is driven predominantly by pressure or the inherent shear that this generates in the sample.
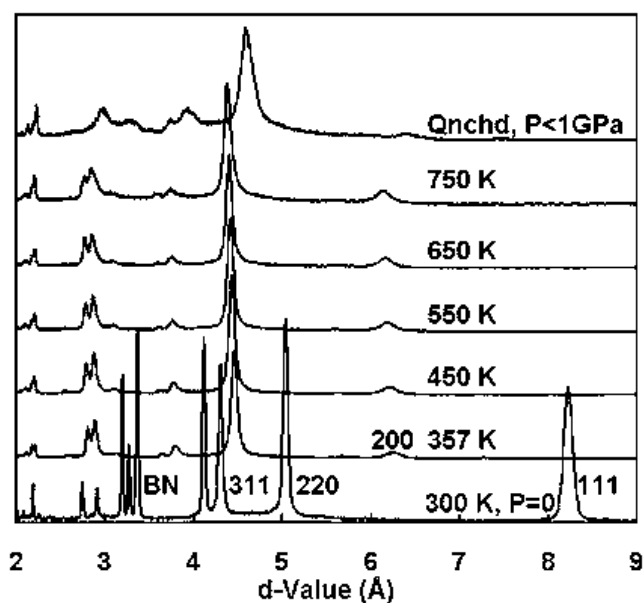
**Figure 1.** The evolution of the XRD trace with temperature at 11.1 GPa.
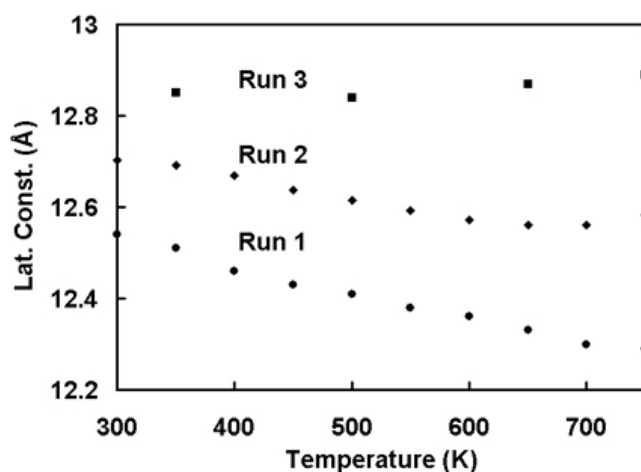


**Figure 2.** The change in lattice parameter with temperature at 11.1 GPa with variations in field isotropy for runs 1 and 2, and at 9 GPa for run 3.

The absence of splitting in the (220) peak would indicate no conversion to 2D tetragonal or rhombohedral polymers. The peak gradually moves towards lower $d$-values that relate to an *in situ* lattice contraction, plotted in figure 2, from 12.54 to 12.28 Å. This correlates to a real contraction, measured from the quenched sample, from 14.16 to 12.95 Å. The reason for the large disparity in unit-cell contraction is that the *in situ* values include thermal expansion whereas the quenched data do not.

Through the whole range of temperatures the XRD traces show an absence of peak splitting in the distorted C$_{60}$ FCC structure, indicating that intermolecular bonding is occurring on average in an isotropic manner unlike 2D polymer formation; if not, we would have loss

of cubic symmetry and hence peak splitting. Thus there do not seem to be any preferential bonding planes or directions unlike in the 2D polymer case. The intermolecular connections are forming in a manner which increases with temperature, and generally average out over the macro-scale resulting in the retention of a pseudo-cubic structure. If we combine this with an extrapolation of the lattice constant graph, the magnitude of bonding increases up to $\sim$800 K where a maximum coordination of 12 is satisfied, correlating with 3D polymer formation, with a lattice constant of 12.25 Å. The FCC structure was still evident after quenching and removal of (all except 0.2 GPa of) the pressure, leading to the conclusion that a pure 3D $C_{60}$ polymer had been synthesized. However, a surprisingly low micro-hardness value of 1.42 GPa, compared with reported values of over 50 GPa, confirms the failure to retain a 3D polymer. Also, the highly plastic character and minimal quantities of elastic recovery indicate the formation of lower-order polymers. It is therefore evident that on the point of final pressure release an unseen phase change has occurred. This previously unreported phenomenon was investigated further using an isotherm in run 4.

To investigate a more anisotropic pressure field, $Al_2O_3$ inserts were introduced prior to a second isobaric run at 11.1 GPa, to increase the shear stress in the die. The new set of spectra follow a trend virtually identical to that for the first set, with a gradual contraction in the pseudo-cubic unit cell as the 3D structure forms with temperature. A similarly low hardness was also found for this sample, indicating the occurrence of analogous phase changes on pressure release. The only noticeable difference between the two is that the lattice contraction occurs to a lesser extent, figure 2, and the quenched sample had a 2.5% larger cubic lattice. This indicates that non-hydrostatic pressure conditions are not conducive to 3D bonding. By arriving at the required conditions via a different history, i.e. an isothermal, ordered 2D polymer route, the problems with molecular free rotation and bonding order can be circumvented. This is discussed for run 4.

The third run was an isobar at 9 GPa, running along the 2D/3D polymer boundary, obtained using a pseudo-isotropic MgO pressure medium. In figure 3, the strong (220) peak does not split or shift, showing retention of the FCC structure and a balance between lattice contraction and thermal expansion. Therefore, bonding processes similar to the 11.1 GPa one are occurring, to a lesser extent, due to the reduction in pressure. However, the (311) peak does show some splitting at low to medium temperatures, indicating that the extremes of the rhombohedral phase field do reach 9 GPa. At just over 1000 K the cages collapse and a phase change occurs over a few minutes, culminating in the diffuse (002) graphitic peak centring at about 3.1 Å. The micro-indentation tests showed the sample to be highly elastic and of a hardness (8.94 GPa) comparable to previously measured values for graphitic 'hard' carbon [15].

History dependence was investigated, with a MgO powder isotherm at 800 K, by forming a 3D phase directly from a 2D phase. In figure 4, with pressure application, the (111) reflection is lost and the (220) and (311) peaks split, indicating the formation of a tetragonal polymer. The phase change from tetragonal to rhombohedral is not distinct, but the already split (311) peak does split further, confirming that these phases can coexist [7–10]. As pressure increases, the shoulder on the (220) peak merges with the main peak as the rhombohedral fraction increases up to 8 GPa. Beyond 8 GPa, all the previously split peaks merge again, resulting in a broad peak indicative of a highly strained FCC polymer. This would indicate that the 2D layers are being 'zipped' together, forming the 3D FCC polymer. The sample was then quenched and the FCC structure remained. However, during the reduction of pressure, although the FCC structure was retained to $\sim$1 GPa, at zero pressure the (220) and (311) peaks suddenly split, reverting back to a mixed phase of 2D/3D polymers or solely 2D polymers. Evidently the strain within the FCC polymer was too great for the intermolecular bonds to hold in the third dimension without the assistance of applied pressure or partial depolymerization into a less strained mixed phase.
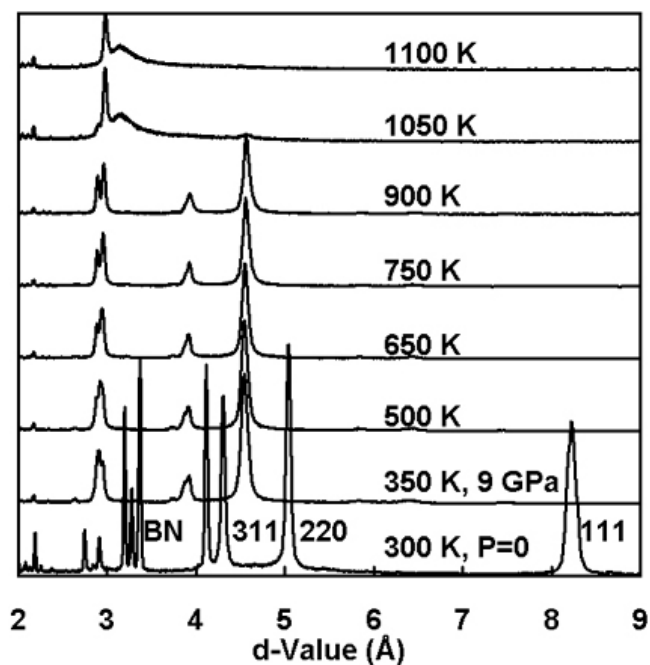
**Figure 3.** The progression of XRD traces with temperature at $P = 9$ GPa.
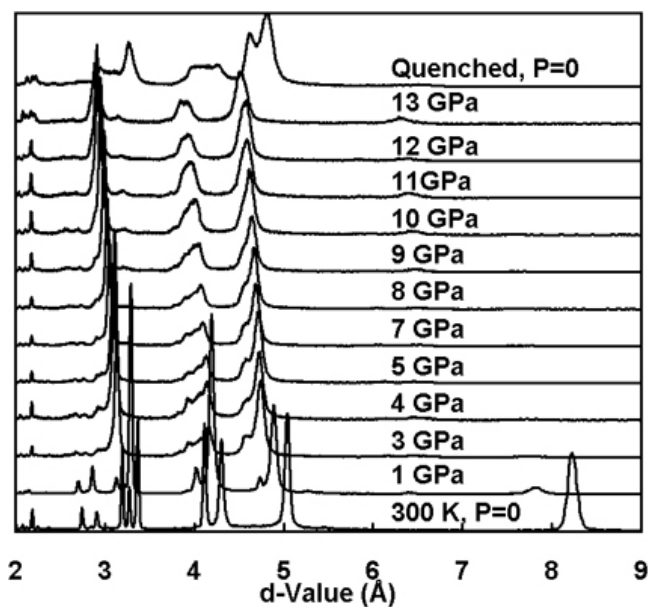


**Figure 4.** Run 4: an isotherm taken at 750 K, $P = 0$–13 GPa.

Raman investigations (figure 5), with the assistance of vibrational spectral assignment [20], gave more insight into the depolymerized product. In the pentagonal pinch region (1400–1470 cm$^{-1}$) there are two peaks overlapping each other. The higher-energy peak at 1440–
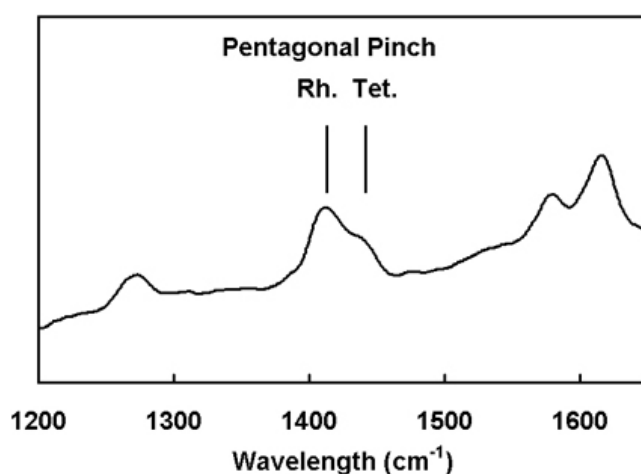
**Figure 5.** The pentagonal pinch region of the Raman spectrum for the quenched Spring-8 run 4 sample.

$1450 \text{ cm}^{-1}$ is the tetragonal pinch and similarly the rhombohedral one is at $1405–1415 \text{ cm}^{-1}$, confirming the presence of both 2D phases. However, the spectrum is more complex than that. The reported intensities of pinch modes in Raman spectra for both of the 2D polymers are characteristically high, but this is evidently not the case here. Bond formation in the third dimension would reduce the proportion of pentagons generating these 'normal' vibrations, resulting in a reduced signal. The extra bonding weakens the pentagon, thus reducing the energy of vibration; this is seen as a downshift of both peaks in the trace. Also the vibrational modes are much broader than the usual sharp peaks in the polymeric trace [18]. This has been documented previously as being indicative of 3D bonding. However, we do not observe this to such an extreme degree. Thus, our Raman trace indicates retention of a limited quantity of the 3D polymer and reversion of the majority of the sample to 2D polymers as a matrix for the 3D micro-domains.

A further experiment entering the 3D field, directly from the pure rhombohedral polymer, was performed to try to overcome this reversion problem. The evolution of XRD traces follows rhombohedral formation, then generation of the FCC with the onset of further polymeric bonding. This unfortunately reverted back on pressure release, however to a lesser extent, and the relative strength of the $(220)_{FCC}$ indicates that a greater proportion was retained. Thus the spatial arrangement of the rhombohedral form generates a more stable, less strained 3D polymer with less tendency to undergo reversion.

Hardness investigations of the last two runs returned disappointingly low values. The micro-hardness and plasticity were both characteristic of soft 2D polymers. This shows that the 2D polymers dominate the sample composition, with domains of the 3D polymer enclosed in a soft 2D phase matrix.

## 4. Conclusions

The $C_{60}$ reaction diagram has now been explored by *in situ* x-ray diffraction experiments below pressures of 13 GPa. It has been shown that at pressures of 11.1 GPa the structure is a strained FCC arrangement with distorted $C_{60}$ cages. The molecules form intermolecular bonds in all directions, reducing the lattice parameter until the strain of forming new bonds cannot

be overcome by the heat and pressure. Less hydrostatic conditions hinder the formation of intermolecular bonds, indicating that conditions of high shear are not conducive to 3D polymer formation. It was confirmed that the boundary between 2D and 3D polymers lies at 9 GPa and cage collapse to form graphitic 'hard' carbon commences at about 1000 K. With a different history the 3D polymer was synthesized *in situ* by 'zipping' together the 2D polymer layers. However, on quenching, the extreme strain in the system could not be accommodated and some domains 'unzipped' themselves, forming more stable lower order polymers. The reclaimed sample was a mixed-phase 2D polymer, with some evidence for retention of FCC 3D polymer micro-domains. This also occurred when forming the 3D polymer from a solely rhombohedral polymer differing only in the relative proportion of 3D polymer contained in the mixed phase.

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