

## Three-dimensional fcc C<sub>60</sub> polymer

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### ABSTRACT

A face-centered cubic (fcc) polymerized C<sub>60</sub> phase has been synthesized at 9.5 GPa and 550 °C. The observed short lattice constant, 13.19 Å, indicates that a three-dimensional (3D) polymer with adjacent C<sub>60</sub> molecules covalently bonded was obtained. Possible polymerized structures, with each molecule adopting one of the two standard orientations, have been investigated through density functional theory (DFT). It was found that intermolecular bonds, 56/56 2 + 2 cycloaddition, are formed between molecules with different orientations but no bonds are formed between molecules with the same orientation. The computed bulk moduli for these structures gave values ranging from 88 to 132 GPa. Although the distances between neighboring molecules and the volume per molecule from the models are close to the experimental values, the relaxed structures displayed symmetries lower than cubic, suggesting that the experimental fcc structure is likely disordered or frustrated.

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## 1. Introduction

At room conditions, C<sub>60</sub> is a Van der Waals solid with a face-centered cubic (fcc) structure, in which the molecules are rotating [1]. When compressed and heated, it forms extended polymerized networks with different dimensionalities and physical properties [2–9]. One-dimensional (1D) orthorhombic and two-dimensional (2D), tetragonal and rhombohedral, phases are synthesized at pressures below 8 GPa. These low-dimensional polymerized phases have a common type of intermolecular covalent bonds, 66/66 2 + 2 cycloadditions, which connects intramolecular double bonds of neighboring molecules [10].

Above 8 GPa, three-dimensional (3D) C<sub>60</sub> polymers are formed. They show outstanding physical properties for pure carbon phases, such as electron conductivity and low-compressibility [2–9]. Furthermore, a very high bulk modulus, superior to that of diamond, has been claimed from C<sub>60</sub> samples subjected to 13 GPa and to temperatures above 700 °C [4].

3D polymeric structures, having exclusively 66/66 2 + 2 cycloaddition bonds, are not possible in ABC-stacked lattices and, thus, new bonding patterns need to be involved in such structures [7]. Previously, we have shown that 3D polymeric structures can

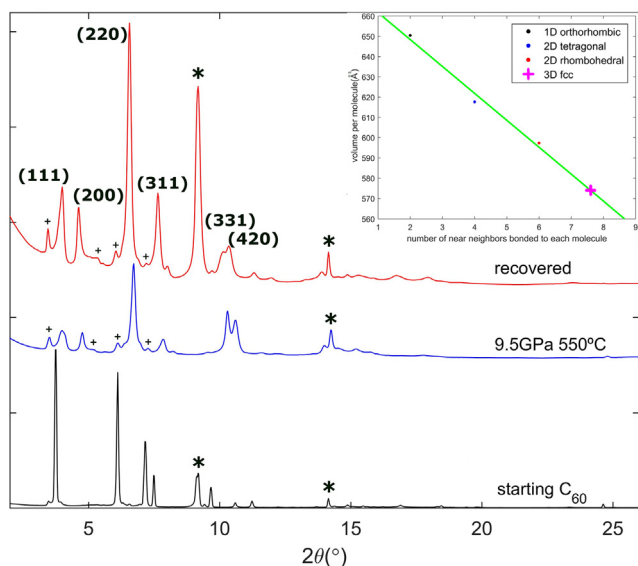
form with 56/56 2 + 2 cycloaddition bonds, which connects intramolecular single bonds of neighboring molecules. Here we present a brief description of our previous works regarding the 3D polymer phase obtained at 9.5 GPa and 550 °C and its possible binary-alloy-type structures [7,8]. In addition, we report the bulk moduli computation for all proposed structures, which are consistent with experimental results.

## 2. Results and discussion

Fig. 1 shows in situ synchrotron diffraction patterns of C<sub>60</sub> under pressure and at room conditions, during the pressure-temperature cycle. The patterns of the transformed sample can be indexed in fcc lattices with constants 12.74 Å, at 9.5 GPa, and 13.19 Å, at room conditions. Experimental details were given elsewhere [7]. In comparison to the starting C<sub>60</sub>, peak shifting to larger 2θ angles, reflecting a compressed structure, and peak broadening are observed for the transformed phase. The low resolution of these diffraction patterns impedes the determination of the detailed crystal structure. Therefore, plane-wave DFT calculations have been performed with VASP package, employing PBE functional, in order to understand the crystal structure of the polymerized phase [11]. Complete details of these computational methods employed were given in reference [8].

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**Fig. 1.** 1D diffraction patterns obtained at different conditions along the pressure-temperature path ( $\lambda = 0.53396 \text{ \AA}$ ). \*: h-BN container diffraction peaks. +: gasket diffraction peaks. Inset: volume per molecule versus number of near-neighbors bonded to each molecule (see text).

In a first step, we have investigated the stability of polymerized structures built with molecules in the standard orientations, since these particular molecular orientations are compatible with the observed cubic symmetry [1]. These models show that no bond is formed by two neighboring molecules with the same orientation but occur under differently oriented molecules via 56/56 2+2 cycloaddition. These intermolecular bonds are analogous to an orientational “antiferromagnetic” interaction and the resulting polymer can be mapped onto an Ising antiferromagnet, where one of the standard orientations corresponds to spin up and the other to the spin down [7]. Similarly, the antiferromagnetic Ising model has also been applied to binary-alloys [12].

By using ordered binary-alloy structures as prototypes, several stable  $C_{60}$  structures have been constructed, shown in Fig. 2, and their stability analyzed [7,8]. Their optimized lattice constants at room conditions are given in Table 1 [8]. Structures 2(a) and 2(b) are analogous to tetragonal AuCuI and rhombohedral CuPt ordered alloy structures and involve orientational “antiferromagnetic” (001) and (111) fcc planes, respectively, which are in turn “ferromagnetically” ordered. The “antiferromagnetic” polymeric bonds are highlighted in red. Each molecule is bonded to eight nearest-neighbors in the AuCuI-type structure and six in the CuPt-type structure. Structure 2(c) is analogous to “ $A_2B_2$ ” structure, consisting of stacked “antiferromagnetic” ordered (001) fcc planes, with each molecule bonded to eight neighbors. Structure 2(d) is analogue to the  $Au_3Cu$  ordered cubic structure, in which less populated molecules bond to their twelve nearest-neighbors while the most populated molecules have four nearest-neighbor bonds. Furthermore, previous DFT calculations show that all these structures present states at the Fermi level and, therefore, they are metallic [8].

All computed structures, excluding the cubic  $Au_3Cu$ -type structure, have lower symmetry than the experimentally observed cubic symmetry and, thus, they cannot be directly assigned to the exper-

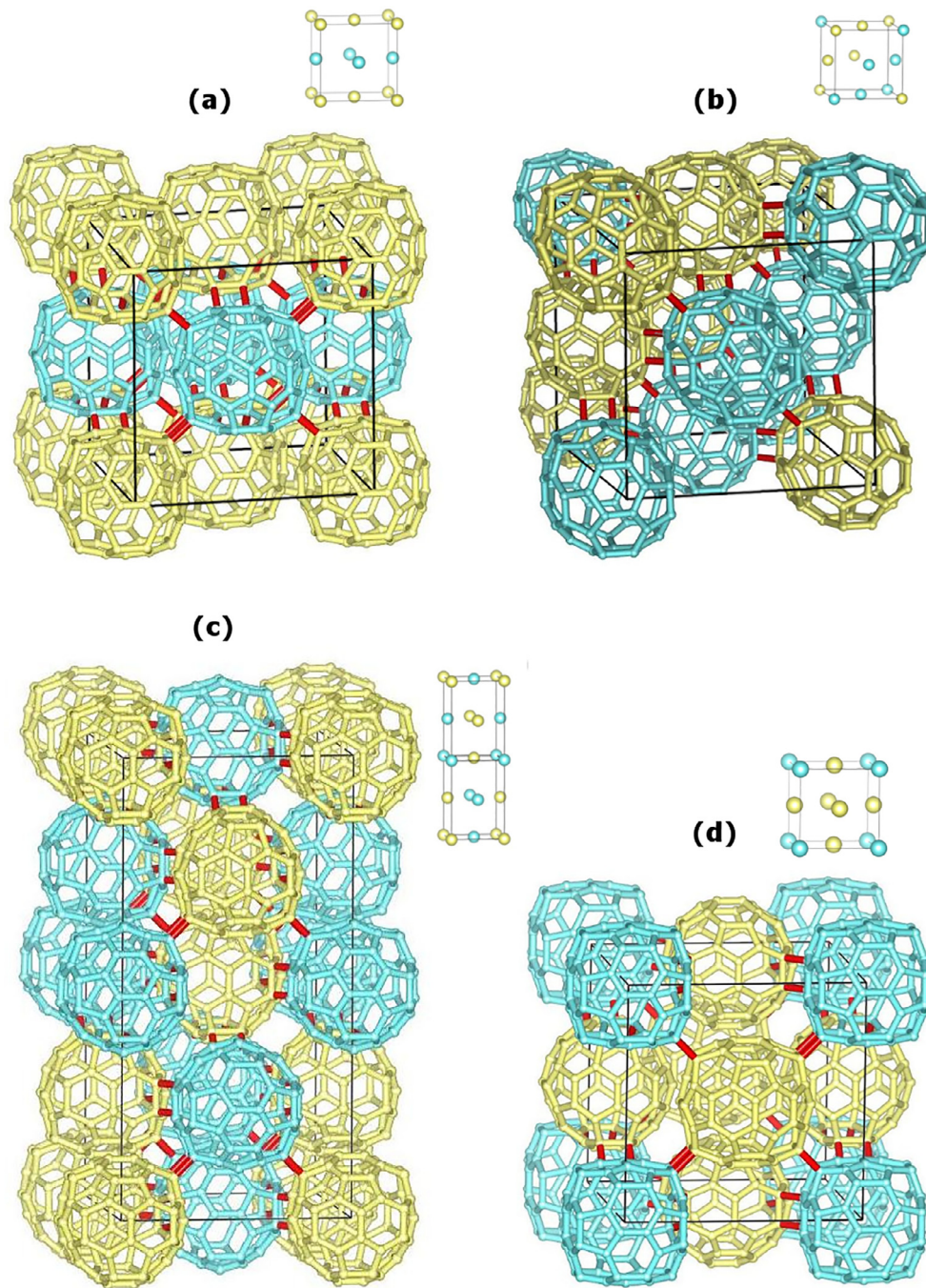
imental phase. Additionally, the  $Au_3Cu$ -type structure must be discarded since it would yield superlattice reflections missing in the experimental pattern. In contrast, the volume per molecule of these structures is close to the experimental one. Indeed, as Talyzin and coworkers pointed out, a linear correlation between the number of bonds per molecule and the volume per molecule is observed for the low-dimensional polymers [13]. Extending this correlation to the volume of the present phase, we obtain an average value of 7.6 molecules directly bonded to each molecule (see inset Fig. 1). This extrapolation can be made with confidence since the polymeric bonds arise all from 2 + 2 cycloadditions. Both AuCuI and “ $A_2B_2$ ”-type structures have eight near-neighbors bonded to each molecule, and their volumes are close to the experimental one. Thus, although we cannot assign the experimental 3D polymerized phase to a single calculated structure, the volume per molecules and also the distance between bonded molecules indicate that the polymeric bond present in the experimental polymerized phase is 56/56 2+2 cycloaddition. The observed cubic symmetry is then the result of disorder or frustrated polymerized structure with a number of bonded near-neighbors of 7.6. Indeed, as we have noted the system can be mapped onto the Ising fcc antiferromagnet, which is naturally frustrated with eight antiferromagnetic bonds per site [12].

Structural optimizations at different pressures were performed to compute the bulk modulus of each structure. The bulk modulus was then calculated by fitting the obtained volumes with the Birch-Murnaghan equation of state (EOS), shown in Fig. 3 [14]. The bulk modulus and its derivative are given in Table 1, for each structure. AuCuI and “ $A_2B_2$ ”-type structures have very similar bulk modulus, around 130GPa, and the same number of polymeric bonds per molecule.  $Au_3Cu$ -type structure has slightly lower bulk modulus, 117 GPa. The CuPt-type structure, with only six polymeric bonds per molecule, has the lowest bulk modulus, 88GPa. Thus, increasing the number of polymeric bonds increases the bulk modulus. An estimation from experimental data can be obtained for pressure-averaged bulk modulus from the molecular volumes at high and ambient pressures. This yields a value of 96GPa, in the range of the computed ones, thus confirming the correctness of bonding type. This range of values is larger than the bulk moduli of the low-dimensional  $C_{60}$  polymers but are smaller than those of 3D  $C_{60}$  polymers obtained at higher pressure [4,5,15]. The rise on the number of polymeric bonds and, concomitantly, on the number of  $sp^3$  carbons, increases, as expected, the bulk moduli displayed by  $C_{60}$  polymers. A value, 217GPa, was reported for an identical 3D fcc polymer but this result is strongly influenced by the large dispersion of the experimental data [13].

### 3. Conclusions

A joint experimental and theoretical study of a 3D  $C_{60}$  polymer obtained at 9.5 GPa and 550 °C, was performed. This polymerized phase has a fcc symmetry with a frustrated structure, where the molecules are bonded through 56/56 2 + 2 cycloaddition.

Based on the 56/56 2 + 2 cycloaddition polymeric bond, several polymerized structures have been constructed and their stability investigated. These structures display bulk moduli ranging from 88 to 132GPa. These values are directly connected to the number of polymeric bonds per molecule, higher number of polymeric bonds leads to higher bulk modulus. Hence, higher pressures should induce more  $sp^3$  bonds leading to even less compressible samples.

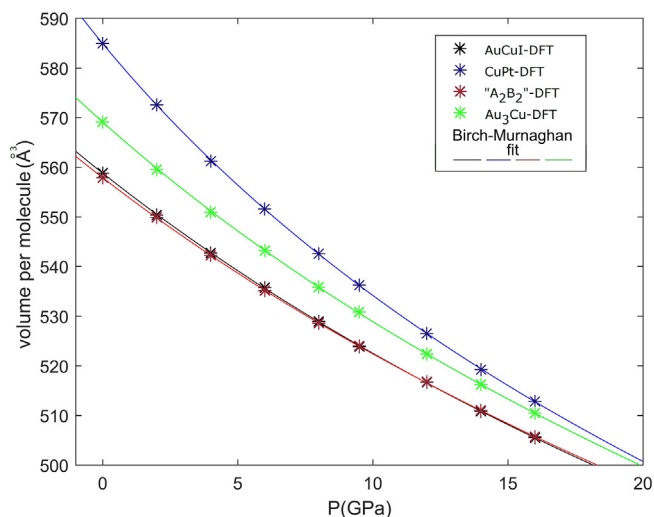


**Fig. 2.**  $C_{60}$  binary-alloy-type structures with binary-alloys as insets. (a) AuCuI-type; (b) CuPt-type; (c) “ $A_2B_2$ ”-type; (d)  $Au_3Cu$ -type. Differently oriented molecules are rendered in yellow/blue and the polymeric bonds are rendered in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Binary-alloy-type structures optimized lattice constants, space group, bulk modulus  $B_0$  and the respective pressure derivative  $B'_0$ .

Alloy-type structure	Lattice constants (Å)	Space group	$B_0$ (GPa)	$B'_0$
AuCuI-type	$a = b = 9.32$ ; $c = 12.87$	$P4_2/mnm$	129.64	4.14
“ $A_2B_2$ ”-type	$a = b = 12.99$ ; $c = 13.22 \times 2$	$I4_1/amd$	132.29	4.25
CuPt-type	$a = b = 9.52$ ; $c = 22.35 \times 2$	$R\bar{3}c$	117.00	4.20
$Au_3Cu$ -type	$a = b = c = 13.15$	$Pm\bar{3}$	88.77	4.76



**Fig. 3.** Birch-Murnaghan EOS fits to calculated volumes per molecule for the different structures (indicated by stars).

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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