Polymerized Fullerite Structures

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We show in this Letter that heating under high pressure drives C_{60} to new distorted crystalline phases that are metastable at room temperature and pressure. We report three different distortions that are essentially characterized by two nearest neighbor distances, $d_0' \sim 10$ and $d_0'' \sim 9.2$ Å. The excellent accord with theoretical calculations supports the view that these new carbon phases can be understood as the long range order polymerization of C_{60} through cycloaddition reactions that are at the origin of the shorter intermolecular distances.

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Since the first synthesis of macroscopic amounts of fullerenes, there have been a number of studies of the behavior at high pressure of C_{60} [1–10]. They were essentially aimed at testing the properties under extreme conditions, i.e., the resilience or breakdown of the C_{60} molecule. The products of the collapsed fullerite phase can be very different: amorphous sp^2 [4,5] carbon or sp^3 carbon [5,6], polycrystalline cubic diamond of small grain size [7,8], microcrystalline graphite [4,5], or unidentified disordered carbon phases [9,10]. Most of these experiments were performed at room temperature or under uncontrolled temperature conditions (shock waves). They have the common limitation that the rapid application of pressure freezes the rotational movements of the buckyballs, forcing a static orientational disorder [11] that prevents transformations to new ordered phases.

On the other hand, it is known that C_{60} can develop cycloaddition reactions of different types. It has been even reported that exposure to light [12] can cause the polymerization of the molecules into clusters of different numbers of molecules. This reaction is reversible, i.e., heating of the polymerized film allows the recovery of pristine C_{60}. It is natural to think that similar reactions can happen in solid C_{60} under pressure at temperatures that prevent the freezing of the C_{60} molecules into an orientationally disordered structure. Indeed some solid state compressed phases that may be formed from polymerized molecules have been recently reported [13,14]. In this Letter we explore the experimental pressure-temperature diagram and compare our results with theoretical calculations of the cohesive properties of structures formed by cycloaddition reactions compatible with the original face centered cubic lattice.

For our experiments we used a belt apparatus capable of applying up to 8 GPa at temperatures below 1500 °C. As received pure C_{60} from MER was previously heated at 220 °C for one week under dynamical vacuum in order to minimize the amount of solvent present in the sample. No special care was taken to avoid contamination with oxygen and the treated soot was kept in air. About 30 mg of C_{60} were encapsulated in a Pt container and compressed in the belt apparatus for periods not exceeding 2 h. We found previously [1] that C_{60} was not stable above 750 °C for the lowest pressure (~2.5 GPa) manageable with our press apparatus, so we started working just below this temperature to maximize the possibility of reaccomodation of the molecules under high pressure.

Cu $K\alpha$ x-ray diffraction patterns of the phases obtained under these conditions are totally different from those found for sp^3 or sp^2 amorphous compounds synthesized at very high pressure [5] but are close to those obtained on fcc or orientationally ordered C_{60}. Typical diffraction patterns are shown in Fig. 1. They could not be indexed on a single cubic, rhombohedric, hexagonal, or tetragonal phase, but the evolution of patterns for different synthesis conditions indicates that we have mixture of two different phases, rhombohedral (R) and tetragonal (T). This assumption was supported by electron diffraction patterns that show that structures of our phases are

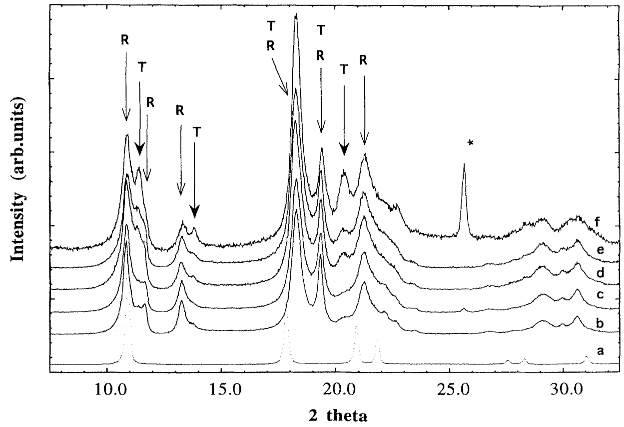

FIG. 1. X-ray diffraction patterns for (a) pristine and (b)–(f) different compressed samples. The evolution of these patterns shows the existence of a secondary phase (tetragonal, T peaks) which coexist with a majority rhombohedral phase (R peaks). * corresponds to an impurity line.

distortions of fcc C_{60} structure having broad reflections, lower symmetry space group, and no superlattice sports. The general intensity distribution of these patterns could be simulated in a first step using the form factor of spherical C_{60} shell, assuming a Lorentzian peak broadening due to small grain size ($\lesssim 500$ Å) . These simulations show that the cage structure is maintained and allow the determination of the molecular positions that are different from those of pristine C_{60} phases. For the samples of Fig. 1 we obtain two phases, whose cell parameters are shown in Table I. The majority one is a rhombohedral phase that results from the compression of (111) fcc planes that was reported previously [13,14]. The minority phase is a tetragonal distortion obtained by a compression of the quadratic (001) fcc planes. In the first case each molecule retains a distance of ~10 Å with only half of the twelve nearest neighbors approaching the other six by 0.8 Å. In the second case the distance to four nearest neighbors molecules is reduced to 9.09 Å (see Table I). The new short distances between molecules are difficult to interpret using nonbonding potentials. Rather, the new value of ~9.2 Å corresponds to theoretical estimations [15] of a polymerization process that proceeds through 2 + 2 cycloaddition of fullerene double bonds. In fact, our samples are insoluble in toluene as photopolymerized C_{60} films. Polymerized C_{60} molecules have been found to convert back to the monomer by thermal annealing at about 200 °C [16]. We have annealed our samples at ambient pressure and at temperatures ranging from 100 to 250 °C. We have verified that the original fcc structure is recovered for short anneals (~2 h) above 200 °C. It thus seems probable that we are dealing with polymerized C_{60} phases.

Although it is easy to propose disordered polymerized clusters of C_{60} molecules, the formation of long range order polymerized phases is severely restricted by symmetry. In the particular case of the precedent phases, we must build up only planes of polymerized molecules, as the distance between molecules of different planes is not affected, and the interactions should remain of van der Waals-type. Considering the geometry of the C_{60} molecule, the simplest possibility for the compressed planes of the rhombohedral and tetragonal phases are the ones shown in the insets *R* and *T* of Fig. 2. The 2 + 2 cycloaddition reaction of double bonds (66/66 bonds) is possible and a ordered polymerized phase can thus be formed for these structures.

Calculations of the structural and energetic properties for these presumed structures have been performed using a tight-binding potential model for carbon [17]. For the rhombohedral phase the calculations predict that the equilibrium intermolecular distance is 9.17 Å, in good agreement with the experimental value.

The relaxed structures show that the fullerene molecules are no longer spheres, but are deformed by the new bonding, and are being elongated along the direction of polymerization. The theoretically obtained carbon atomic positions were used to perform x-ray pattern simulations. Allowing for a slight cell parameter scaling, we found that in both the rhombohedral and the tetragonal phase they

Table I. Structural parameters of the compressed fullerite phases.

Phases	Cell parameters/Å	Distance between centers of molecules/Å	Volume/ molecule Å^3
Pristine	$a = 14.17$	10.02	711
Rhombohedral	$a = 9.19$	9.20	597
	$c = 24.50$	9.74	
Tetragonal	$a = b = 9.09$	9.09	618
	$c = 14.95$	9.86	
Orthorhombic	$a = 9.26$	9.26	650
	$b = 9.88$	9.88	
	$c = 14.22$	9.82	

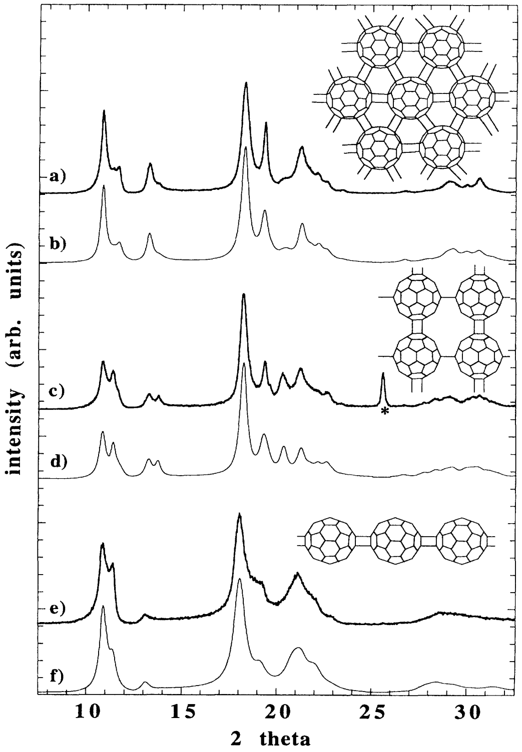

FIG. 2. X-ray diffraction patterns (thick lines) and simulations (thin lines) for (a) an almost pure rhombohedral phase, (b) a mixture of rhombohedral and tetragonal phases (* corresponds to an impurity line), and (c) a pure orthorhombic phase. The structural models of the rhombohedral (*R*), tetragonal (*T*), and orthorhombic (*O*) phases are also shown.

give a much better agreement with the experimental patterns than those calculated using a uniform spherical shell model, indicating that our phases can be explained by the polymerization of C_{60} molecules. An additional improvement was obtained by introducing a merohedral twinning corresponding to molecular disorder. In Fig. 2(a), we show the best simulation of an experimental pattern corresponding to a sample that is an almost pure rhombohedral phase (82% R, 18% T) synthesized at 4 GPa and 700 °C. In Fig. 2(b), we give the simulation of the experimental pattern corresponding to a mixed sample (65% R, 35% T) obtained at 3 GPa and 600 °C. Although the relaxed theoretical structure is an orthorhombic one, stacking disorder to 2D (100) planes induces a smearing of a and b parameters, giving rise to a macroscopic tetragonal structure. The atomic coordinates used in the x-ray patterns are shown in Table II.

Working at higher pressures and lower temperatures (8 GPa, 300 °C), we have obtained a third phase (Tables I and II). Our analysis leads to a one-dimensional polymerization of C_{60} molecules as it was previously observed on K_1C_{60} or Rb_1C_{60} [18,19]. The experimental x-ray powder pattern together with the best simulation are shown in Fig. 2(c). In this case, a better agreement is obtained using uniform spherical shells, instead of the relaxed theoretical positions. This is possibly explained by the fact that the libration degrees of freedom are quenched only along the chain axis, giving rise to a pseudouniform spherical atomic distribution. The spectra of this phase is close to the one of the compressed fcc phase of Iwasa

TABLE II. Atomic coordinates used in the x-ray pattern simulations.

Rhombohedral phase				
Lattice constants	$a = 9.19$ Å, $c = 24.5$ Å (hexagonal cell)			
Space group	$R\bar{3}m$			
Atomic coordinates	C1	0.361	0.456	0.012
	C2	0.450	0.225	0.024
	C3	0.274	0.391	0.065
	C4	0.380	0.190	0.075
	C5	0.292	0.016	0.096
	C6	0.155	0.157	0.130
C1-C1 interfullerene distance 1.68 Å				
C1-C1 intrafullerene distance 1.60 Å				
C1-C2 and C1-C3 intrafullerene distance 1.51 Å				
Other C-C distances remain in the range 1.37–1.47 Å				
Tetragonal phase				
Lattice constants	$a = 9.09$ Å, $c = 14.95$ Å			
Space group	$Immm$			
Atomic coordinates	C1	0.410	0.089	0.000
	C2	0.252	0.286	0.049
	C3	0.000	0.410	0.054
	C4	0.334	0.161	0.079
	C5	0.130	0.335	0.097
	C6	0.287	0.082	0.153
	C7	0.079	0.254	0.173
	C8	0.157	0.129	0.202
	C9	0.077	0.000	0.232
C1-C1 interfullerene distance 1.64 Å				
C1-C1 intrafullerene distance 1.63 Å				
Other C-C distances remain in the range 1.37–1.47 Å				
Orthorhombic phase				
Lattice constants	$a = 9.26$ Å, $b = 9.88$ Å, $c = 14.22$ Å			
Space group	$Immm$			
Molecular center positions	0, 0, 0, and 1/2, 1/2, 1/2			
Molecular radius	3.55 Å			

et al. [14]. However, the diffuse scattering that exists in our sample between 19° and 20° is only accounted for by introducing the orthorhombic distortion.

Although our measurements do not allow an unambiguous structural determination, the agreement between the measured spectra with the simulations obtained using the relaxed atomic positions issued from the theoretical calculations clearly indicates that C_{60} molecules are polymerized by moderately high compressions at high temperatures. The three obtained structures may be the first of a rich variety of new carbon phases with potentially interesting properties.

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