PHYSICAL REVIEW B VOLUME 54, NUMBER 18 1 NOVEMBER 1996-II

Pressure and temperature diagram of polymerized fullerite

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(Received 18 July 1996)

We have systematically studied the temperature-pressure diagram of C_{60} at pressures between 37 kbar and 80 kbar and from room temperature to 900 °C. We show here the specific role played by the temperature in the phase transformations observed in the *P-T* region covered by this study. As temperature is increased, we follow the continuous transformation of fcc fullerite to an orthorhombic phase of polymerized C_{60} chains that, at higher temperature, polymerize to two-dimensional C_{60} polymers. Above 800 –900 °C the C_{60} cage collapses with formation of an sp^2 amorphous phase. The continuous evolution of the x-ray patterns during these phase transformations is explained on the basis of a *homogeneous* solid-state polymerization. [S0163-1829(96)50742-3]

Many reports on C_{60} studies at high pressure have been published since C_{60} became available in macroscopic amounts. These studies were aimed at probing the cage structure stability and looking for eventual new structures.[1] In particular, it has been shown that C_{60} could be transformed under pressure into the other carbon polymorphs, diamond and graphite.[2]

Recently we and others have found new metastable C_{60} phases at moderately high pressures and temperatures, where the C_{60} cage is conserved.[3–5] Spectroscopic results and tight binding calculations coupled with diffraction data show that these new phases are C_{60} polymers, where the C_{60} monomers are linked through a 2,2 cycloaddition reaction.[4–6] Three phases were fully characterized.[4,6] An orthorhombic body centered one, found at 300 °C and 80 kbar, is formed by C_{60}-based chains one-dimensional (1D), similar to those present in one phase of the RbC_{60} compound.[7] At higher temperatures and lower pressures, two other phases made of two-dimensional (2D) polymerized layers were identified: a pseudobody centered tetragonal phase containing quadratic polymerized layers and a rhombohedral phase with an *ABC* packing of hexagonal polymerized layers. Recent NMR measurements on the rhombohedral phase detect six inequivalent carbon atoms and confirm both the structural model proposed for this polymer and the cycloaddition reaction as the polymerization reaction.[8] These results proved that the pure C_{60} polymers can be synthesized from solid precursors, in contrast to solution-phase routes that up to now have failed to produce pure C_{60} polymers.

In order to study the influence of pressure and temperature in the formation and stabilization of these phases as well as to test the possibility of structural connections between them, we have scanned the *P-T* region where these polymerized phases are encountered.

Each sample was made by encapsulating approximately 20 mg of C_{60}, provided by Bucky USA, in Pt containers. As the results are sensitive to the path and the reaction time, all the reported results were obtained with the same protocol. The capsules were compressed, in a belt apparatus type, to the desired pressure over a 1 h period, then the temperature was ramped for 20 min and held for 1 h at the reaction temperature. Subsequently, the temperature was quenched to room temperature in 5 min followed by a gradual pressure release over 1 h. The diffraction patterns of the recovered samples were obtained with a Siemens D5000 (Cu $K\alpha$) diffractometer using a Bragg-Brentano geometry.

Figure 1(a) shows the diffraction patterns of samples compressed at 48 kbar and different temperatures. The diffraction pattern of the sample compressed at room temperature is that of fcc C_{60}, but with broader peaks denoting some disorder. For the 50 °C sample we already observe an orthorhombic distortion, which persists with a continuous shift of the position of the peaks (lattice parameters) till 250 °C. The 250 °C sample pattern was indexed in a orthorhombic body centered cell with lattice parameters $a = 9.24$ Å, $b = 9.89$ Å, $c = 14.25$ Å. This structure corresponds to the reported 1D C_{60} polymer.[4] At 300 °C a peak emerges at $2\theta \cong 19°$ and additional structure appears at $2\theta \cong 30°$. At higher temperatures these new features are growing in intensity while the maximum of the peaks continues to shift. At 600 °C we have a less disordered sample, whose pattern may be totally indexed in a rhombohedral lattice with hexagonal cell parameters $a = 9.19$ Å and $c = 24.50$ Å. This structure corresponds to the reported 2D-rhombohedral C_{60} polymer.[4] Increasing once more the temperature makes the peaks to become broader. At approximately 850 °C the cage structure is destroyed with formation of an amorphous sp^2 phase, as described previously.[2]

It is known from solid-state polymerization studies that there are two different processes by which a polymer can grow in a monomer matrix:[9]

(a) *heterogeneous*—the polymer grows in aggregates and both the polymer and the monomer phases can be identified from the diffraction patterns.

(b) *homogeneous*—the polymer chains grow randomly inside the monomer matrix, the diffraction pattern presents a continuous change in cell parameters and symmetry, as in a solid solution.

As the differences between the patterns of the recovered C_{60} are subtle, we have carefully taken all of them at the same conditions. In order to have a correct 2θ normalization, we use as reference a Bragg peak displayed by the sample support, which is present in all spectra. With all of these experimental precautions, we have analyzed the polymerization process by a comparative study of the patterns displayed by the different recovered samples.

As seen in Fig. 1(a) a continuous evolution of the patterns appears from room temperature till 250 °C where we have a complete 1D polymerization. The intermediate patterns cannot be interpreted in terms of coexistence of the orthorhombic plus the fcc phase. As shown from Fig. 1(b) the peak shift is real and we observe no shoulders on our peaks; furthermore the fcc peaks have disappeared completely and no fcc phase was detected by differential scanning calorimetry measurements.[10] Thus the pattern evolution is single phased as in a solid solution and we have a homogeneous solid-state polymerization process where the C_{60} chains grow at random in a fcc C_{60} matrix.

From 250 to 600 °C the orthorhombic x-ray pattern evolves continuously into the rhombohedral phase as in a solid solution. We can once more think in terms of a homogenous polymerization where now the 2D polymerized hexagonal layers grow randomly inside the 1D chain matrix. Nevertheless we cannot determine unambiguously which polymerization process governs the 2D polymer growth. For these two phases, orthorhombic 1D and rhombohedral 2D, the peak widths are large and the peak positions are close. Hence the possibility of peak overlap that would correspond to an heterogeneous polymerization, can also describe the x-ray pattern evolution.

It must be emphasized that up to now all the orthorhombic samples that we have obtained, present, both from our x-ray spectra and from NMR measurements,[8] a much higher degree of disorder than the rhombohedral samples. The disorder, calculated from the peak width, is for the rhombohedral sample about half that of the orthorhombic one. We may understand it by the fact that 1D C_{60} polymers are more prone to disorder, like chain orientational disorder (static and/or dynamic) or staggered chain deformation, than the 2D C_{60} polymer.

Temperature is essential both in obtaining the polymerized phases and in selecting the 1D or the 2D polymer. It is also mainly responsible for the breakdown of the C_{60} cage. It has been shown that the dynamical disorder (provided by temperature) is essential for photopolymerization to be accomplished.[11] The free molecular rotations are important because they allow the correct molecular orientation for the polymerization reaction to occur (in the 2,2 cycloaddition reaction the double bonds of adjacent molecules must be face-to-face). The importance of this factor in the polymerization process under high pressure-high temperature (HPTP) has already been pointed out.[12] However, as shown by extrapolating the dependence of the order-disorder transition temperature versus pressure for pristine C_{60},[13] it is surprising that polymerized phases can be obtained for P-T values that do not allow rotation of the molecules,[12] in contrast to the photopolymerization process. We suggest that in this case molecular oscillations may be sufficient to provide the correct molecular orientation for the polymerization reaction. It is known that the molecular orientation favored under pressure is the one that has an hexagon of one molecule facing a double bond of the nearest neighbor molecule.[14] In this configuration low amplitude librations are enough for the molecule to accede to the correct molecular orientations for cycloaddition reaction, but only in certain directions leading to long-range order C_{60} polymers. As in belt-type press experiments the pressure is applied before temperature, the polymerization will always start in the way explained above, in a region where the molecules are nonrotating. In agreement with this suggestion, we have found that the long-range order polymerization only takes place around $\geqslant 10$ kbar,[15] which is the pressure where the proportion of

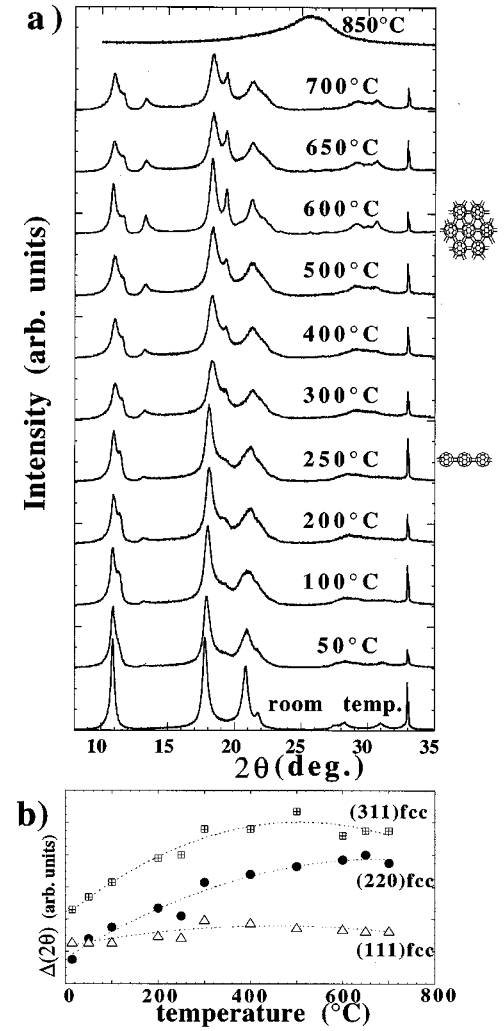

FIG. 1. (a) X-ray diffraction patterns for C_{60} compressed at 48 kbar and heated at different temperatures. The sharp peak at nearly 33° (2θ) is due to the sample holder used in x-ray measurements. (b) Relative peak shift (2θ) evolution of the three principal fcc C_{60} reflections during the phase transformations.

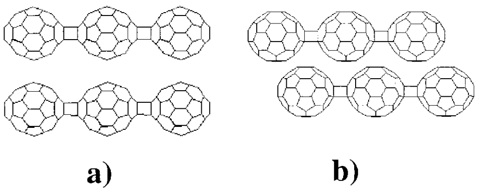

FIG. 2. Scheme of C_{60} chains associations in order to form (a) quadratic and (b) hexagonal polymerized layers.

hexagon facing double bond orientation reaches almost 100%.[14] On the contrary, for the photopolymerization, which occurs only if the molecules are free to rotate, the probability that two molecules have the correct orientation for the polymerization reaction is the same in any direction. The polymerization, in this case, takes place in all directions and an amorphous rather than an ordered polymer will be formed.[11]

In HPHT polymerization, and in contrast to photopolymerization process, the temperature plays also another role, by providing the energy necessary for the polymerization reaction. The 2,2 cycloaddition reaction is said to be thermally forbidden because the potential barrier is too large to be overcome only by thermal energy.[16] However, at high pressures this barrier is lowered and the process is now thermally allowed.[17] The tight binding calculations have shown that the energies (temperatures) needed to polymerize 1D and 2D are different, because more covalent bonds are formed in the 2D case.[6] Hence with increasing temperature the number of bonds increases, and the average length of the chain grows, in agreement with the x-ray diffraction patterns evolution of Fig. 1. At higher temperature, there is enough thermal energy to overcome the potential barrier and form the 2D polymer. At the same time, the chains will be able to oscillate more loosely increasing the probability of having the correct molecular orientation to create covalent bonds between them. In order to form hexagonal polymerized layers, the chains must approach each other along the (001) (⟨100⟩ is the polymerization direction) body centered orthorhombic planes, with the relative molecular orientations shown in Fig. 2(b), and each molecule is linked covalently to six neighbors. For temperatures above 600 °C, there is a weak increase of the peak widths. At 800–900 °C the cage structure is destroyed and the recovered product is the sp^2 amorphous phase.[2] It seems that around this critical temperature bond variations become overwhelmingly strong resulting in a cage structure collapse, as at ambient pressure.[18]

In most of the range reported herein, the influence of pressure magnitude in the polymerization process is less selective than that of temperature. Samples obtained at the same temperatures, but different pressures present nearly the same diffraction patterns. This is not valid, however, for higher temperatures, where we can see a minority new tetragonal phase (Fig. 3) formed at lower pressure, competing with the rhombohedral phase. At the same temperature and higher pressures only the rhombohedral phase is present. The tetragonal phase is also a 2D polymer with a pseudobody centered tetragonal lattice composed of 2D quadratic polymerized layers.[4] It is less compressed than the rhombohedral one (volume available per molecule is approximately 620 Å^3 against 600 Å^3 for the rhombohedral phase), explaining why we obtain it at lower pressure values. In the tetragonal phase each molecule is linked covalently to four molecules as the chains approach each other in the orthorhombic (001) planes [Fig. 2(a)]. This suggests that at lower values of pressure the 2D stable phase is the tetragonal one and for lowest pressures we find the 1D orthorhombic, the less compressed phase.[15] It is interesting to compare the volume available to one molecule in each of the compressed phases with the cell volume changes under pressure at room temperature measured *in situ* by Duclos *et al.*[19] The pressures needed to compress C_{60} at room temperature to the volumes corresponding to rhombohedral, tetragonal, and orthorhombic phases are respectively 50, 40, and 25 kbar. The temperature is important since it allows the covalent bonding between molecules that stabilizes the compressed phases after releasing the pressure. Therefore, at high temperatures where all the possible bonds are formed, we note that at pressures of about 50 kbar we encounter the rhombohedral and that below 40 kbar the tetragonal phase begins to appear, in agreement with the Duclos results. In this sense the orthorhombic 1D polymer phases obtained in these experiments, due to the low values of the temperature synthesis, are frustrated structures where not all the possible intermolecular covalent bonds are formed. At larger pressures (not covered by this study) and temperatures it is possible to find new highly compressed, 3D polymer phases, with a majority of sp^3 hybridized carbons.[20] The very hard phases obtained by submitting C_{60} at 130 kbar and different temperatures, may indeed be an example of this polymerized 3D structures.[21]

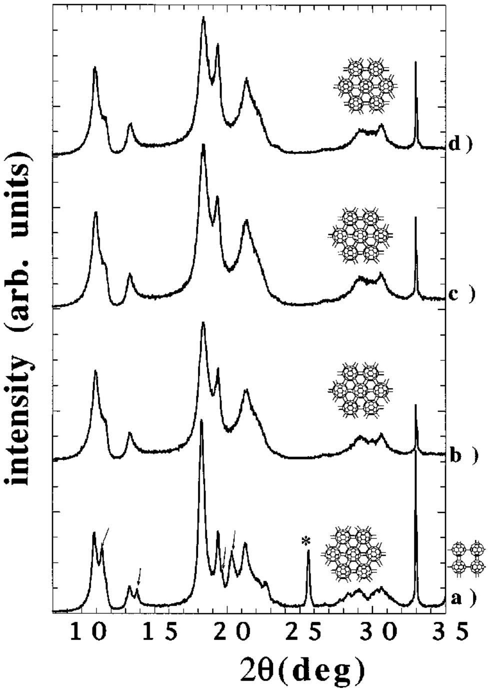

FIG. 3. X-ray diffraction patterns for C_{60} heated at 700 °C and compressed at (a) 37 kbar, (b) 50 kbar, (c) 60 kbar, and (d) 80 kbar. The arrows indicated the peaks arising due to the tetragonal phase. The peak * is an impurity reflection and the sharp peak at nearly 33° (2θ) is due to the sample holder used in x-ray measurements.

The frontier line that bounds the amorphous sp^2 region in Fig. 4 is pressure dependent. We can understand this by the fact that at the same temperature the bonds vibrate more for

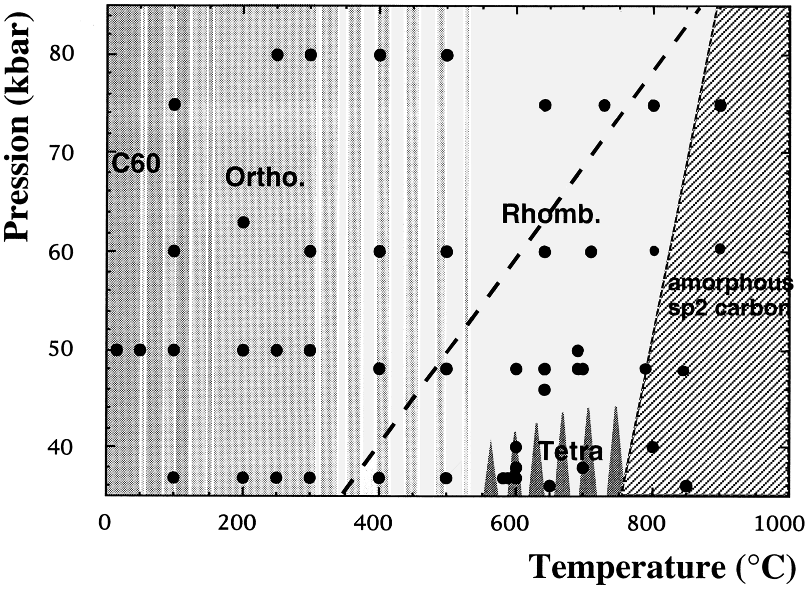

FIG. 4. Pressure-temperature diagram of C_{60}. The intermittent shaded areas correspond to the phases evolution discussed in the text. At lower pressures and higher temperature there is coexistence of the 2D polymerized competing phases, rhombohedral plus tetragonal. The broken line represents the extrapolation of order-disorder temperature versus pressure curve for the C_{60}, according to Ref. 13.

lower pressure, and therefore at higher pressures we must increase the temperature to produce the same critical vibrational amplitude that destroys the cage structure. It must be emphasized that the amorphous sp^2 samples that we obtained close to the frontier are harder than normal graphite as it was remarked before.[22] Though an average graphitic structure is observed by x-ray diffraction,[2] it could be possible that some of the graphene planes are connected by covalent bonds through the remaining pentagons.[23] We must also note that at room temperature and very high pressure, 200 kbar, the cage structure collapses giving rise to entirely sp^3 crystalline or amorphous samples.[24]

In conclusion, we present the P-T diagram for C_{60} describing the regions where the polymerized fullerite phases can be synthesized. In our range of pressures, the temperature is the key parameter that selects the synthesis of the 1D or 2D polymers or the transformation to an amorphous sp^2 phase. The pressure parameter is less selective, but it influences the rate of formation of the two competing 2D polymers. We found that the absence of molecular rotation at the beginning of polymer growth is crucial in obtaining the long-range order polymers, because it restricts the number of the directions of polymerization inside the C_{60} monomer matrix, in contrast to photopolymerization process. From the analysis addressed here we can anticipate that at high pressures ($>$80 kbar) highly compressed 3D C_{60} polymer phases, with a majority of sp^3 carbons, probably could be obtained.

L.M. was supported by JNICT, Lisbon, Portugal.

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