Raman Modes and Stability at High Pressure of the Two-Dimensional Rhombohedral Polymer of C$_{60}$

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ABSTRACT

Phonon modes and stability of the planar rhombohedral polymer of C$_{60}$ have been studied at pressure up to $\sim$30 GPa by means of in situ Raman scattering. At $P \sim 15$ GPa the phonon frequencies show an irreversible transition to a new phase related with random covalent bonding between the molecules in adjacent polymeric sheets.

Key Words: Phonon modes; Raman scattering; Rhombohedral polymer; C$_{60}$.

The treatment of C$_{60}$ under high pressure and high temperature leads to its polymerization related to the intermolecular covalent bonding via $sp^3$-like
coordinated carbon atoms. The crystal structures of polymers have been identified as one-dimensional orthorhombic (1D-O), two-dimensional tetragonal (2D-T) and rhombohedral (2D-R), and three-dimensional face-centered cubic.\(^\text{[1–3]}\) The number of \(sp^3\)-like coordinated atoms per \(C_{60}\) cage increases from 4 to 8 and to 12 for 1D-O, 2D-T, and 2D-R phases, respectively. Theoretical studies\(^\text{[4,5]}\) have predicted that uniaxial compression of the 1D or 2D polymers leads to 3D polymerization with 24, 52, 56, and even 60 \(sp^3\)-like coordinated atoms per \(C_{60}\) cage. Raman studies of the 2D-T polymer at high pressure have revealed irreversible transition near 20 GPa,\(^\text{[6]}\) related to its polymerization in accordance with.\(^\text{[4]}\) In this communication we report the pressure-induced transformations of the 2D-R polymer studied by means of in situ Raman scattering at pressure up to \(\sim 30\) GPa.

The 2D-R polymer was obtained by subjecting 99.99% pure \(C_{60}\) powder to a pressure of \(P \sim 5\) GPa at a temperature of 773 K. The X-ray analysis confirmed the rhombohedral crystal structure (space group: \(R\overline{3}m\), \(a = 9.22\) Å and \(c = 24.6\) Å).\(^\text{[1]}\) Raman measurements at high pressure were carried out using a diamond anvil cell of Mao-Bell type and a triple monochromator.

\[\text{Figure 1. Raman spectra of the 2D-R polymer at room temperature and various pressures.}\]
The Raman spectra of the 2D-R polymer recorded under pressure increase from 0.9 to 30 GPa and then back to 0.5 GPa are shown in Fig. 1. As the pressure increases, the Raman peaks shift to higher energies and their bandwidth gradually increases. Irreversible changes take place at ~15 GPa when the Raman spectrum becomes very diffuse. The transition is preceded by rapid decrease in the intensity of the $A_g(2)$ “pentagonal pinch” (PP) mode. Figure 2 shows the pressure behavior of the Raman modes in the energy region 1370–1710 cm$^{-1}$. To reveal the contribution of imperfections in the broadening of bands we have annealed the recovered samples at $T \geq 600$ K. The Raman spectra of the annealed sample show transformation of material to a mixture, containing monomers and dimers of C$_{60}$ (insert in Fig. 2).

The pre-transitional decrease of the PP-mode intensity is associated with destruction of double C=C bonds and creation of covalent intermolecular links. Even though pressure decreases preferentially the interplane distance of

![Figure 2](image-url)

**Figure 2.** The pressure dependence of the Raman modes of the 2D-R polymer. Circles (squares) represent the initial phase (high-pressure phase), open (solid) symbols show increasing (decreasing) pressure runs. Shaded area denotes the pressure range of the transformation. Insert: Raman spectra of the 2D-R polymer and of the recovered sample. (a) The initial 2D-R polymeric phase. (b) The “high-pressure” phase. (c) The “high-pressure” phase after being annealed.
the 2D-R polymer, C\textsubscript{60} molecules belonging to adjacent polymeric sheets do not have optimal relative orientations for the covalent bonding. So, we may assume that the new bonds are formed in a random way due to some distortion in the molecular orientations. As a result, the new high-pressure phase exhibits a degree of disorder related to a random out-of-plane polymerization.

Finally, the quenching of PP-mode, the retention of molecular cage and the irreversibility of transition are the indications that a new high-pressure phase of the 2D-R polymer may be related with the 3D cross-linked polymerized C\textsubscript{60}.

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