Downloaded By: [HEAL-Link Consortium] At: 16:01 14 January 2008

FULLERENES, NANOTUBES, AND CARBON NANOSTRUCTURES
Vol. 12, Nos. 1 & 2, pp. 301–304, 2004

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

K. P. Meletov*

Institute of Solid State Physics, RAS, Chernogolovka,
Moscow Region, Russia

ABSTRACT

Phonon modes and stability of the planar rhombohedral polymer of C_{60} have been studied at pressure up to ~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

---

*Correspondence: K. P. Meletov, Institute of Solid State Physics, RAS, 142432 Chernogolovka, Moscow Region, Russia; E-mail: mele@issp.ac.ru.

DOI: 10.1081/FST-120027219 1536-383X (Print); 1536-4046 (Online)
Copyright © 2004 by Marcel Dekker, Inc.
www.dekker.com

ORDER REPRINTS

Downloaded By: [HEAL-Link Consortium] At: 16:01 14 January 2008

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.[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[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,[6] related to its polymerization in accordance with.[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 ~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: $R\bar{3}m$, $a = 9.22$ Å and $c = 24.6$ Å).[1] Raman measurements at high pressure were carried out using a diamond anvil cell of Mao-Bell type and a triple monochromator.

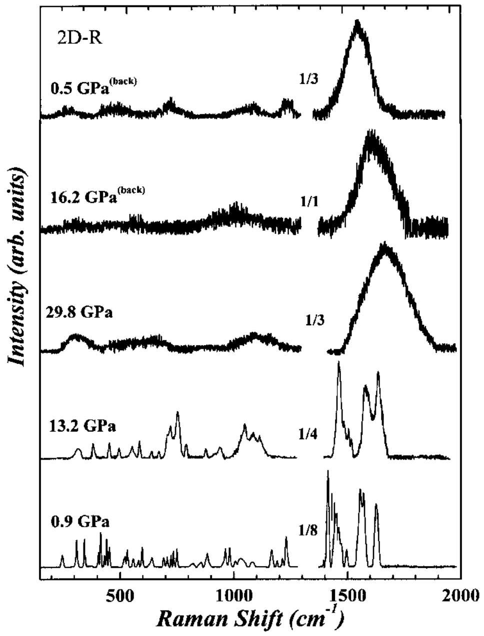

Figure 1. Raman spectra of the 2D-R polymer at room temperature and various pressures.

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

Downloaded By: [HEAL-Link Consortium] At: 16:01 14 January 2008

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

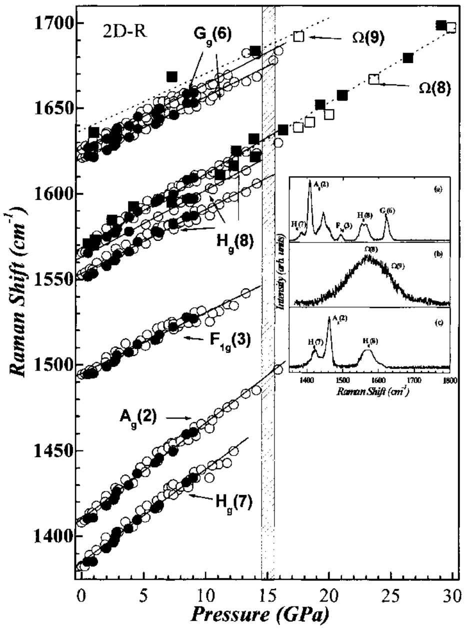

Figure 2. The pressure dependence of the Raman modes of the 2D-R polymer. Circles (squares) represent the initial phase (high-pressure phase), open (solid) symbols show increasing (decreasing) pressure runs. Shaded area denotes the pressure range of the transformation. Insert: Raman spectra of the 2D-R 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.

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

Downloaded By: [HEAL-Link Consortium] At: 16:01 14 January 2008

the 2D-R polymer, C_{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_{60}.

ACKNOWLEDGMENTS

The support by the Russian Foundation for Fundamental Research, grant #03-02-16011, and the support by the Russian State Research Program "Physical properties of the carbon-based nanostructures and development of a new electronic devices" is gratefully acknowledged.

REFERENCES

1. Iwasa, Y.; Arima, T.; Fleming, R.M.; Siegrist, T.; Zhou, O.; Haddon, R.C.; Rothberg, L.J.; Lyon, K.B.; Carter, H.L., Jr.; Hebard, A.F.; Tycko, R.; Dabbagh, G.; Krajewski, J.J.; Thomas, G.A.; Yagi, T. New phases of C_{60} synthesized at high pressure. Science **1994**, *264*, 1570–1572.
2. Nunez-Rugueiro, M.; Marques, L.; Hodeau, J.-L.; Bethoux, O.; Perroux, M. Polymerized fullerite structures. Phys. Rev. Letters **1995**, *74*, 278–281.
3. Brazhkin, V.V.; Lyapin, A.G.; Popova, S.V. Mechanism of three-dimensional polymerization of fullerite C_{60} at high pressure. JETP Letters **1996**, *64*, 802–807.
4. Okada, S.; Saito, S.; Oshiyama, A. New metallic crystalline carbon: three dimensionally polymerized C_{60} fullerite. Phys. Rev. Letters **1999**, *83*, 1986–1989.
5. Burgos, E.; Halac, E.; Weht, R.; Bonadeo, H.; Artacho, E.; Ordejon, P. New superhard phases for three-dimensional C_{60}-based fullerites. Phys. Rev. Letters **2000**, *85*, 2328–2331.
6. Meletov, K.P.; Assimopolous, S.; Tsilika, I.; Kourouklis, G.A.; Arvanitidis, J.; Ves, S.; Sundqvist, B.; Wäberg, T. High-pressure induced metastable phase in tetragonal 2D polymeric phase of C_{60}. Chem. Phys. Letters **2001**, *341*, 435–441.

Submitted July 4, 2003
Accepted August 10, 2003

Copyright © Marcel Dekker, Inc. All rights reserved.