

phys. stat. sol. (b) **223**, 489 (2001)

Subject classification: 61.48.+c; 62.50.+p; 78.30.Na; S5

High-Pressure Phase in Tetragonal Two-Dimensional Polymeric C₆₀

K. P. MELETOV¹) (a, b), J. ARVANITIDIS (c), S. VES (c), and G. A. KOUROUKLIS (a)

(a) *Physics Division, School of Technology, Aristotle University of Thessaloniki, GR-54006 Thessaloniki, Greece*

(b) *Institute of Solid State Physics of the Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia*

(c) *Physics Department, Aristotle University of Thessaloniki, GR-540 06 Thessaloniki, Greece*

(Received July 27, 2000)

The pressure behavior of the phonon modes of tetragonal two-dimensional polymeric C₆₀ has been studied at pressure up to 27.5 GPa and room temperature by means of Raman spectroscopy. Gradual transformation of the material to a new phase was observed in the pressure region 18.0–22.0 GPa. The Raman spectrum characteristics of the high-pressure phase provide a strong indication that the fullerene molecular cage is retained and the material may be related to a three-dimensionally polymerized C₆₀. The new phase remains stable upon pressure decrease down to 9 GPa. Further release of pressure leads to its transformation to a highly disordered structure whose broad features in the Raman spectrum resemble those of amorphous carbon.

Introduction A variety of phases of polymerized fullerites have been synthesized starting from the pristine C₆₀ material under high pressure and high temperature treatment [1–3]. The crystal structures of these polymeric phases have been identified as one-dimensional orthorhombic [2], two-dimensional tetragonal [2], and two-dimensional rhombohedral phases [1, 2]. The polymerization is attained by the so-called (2 + 2) cyclo-addition mechanism via the formation of four-membered rings between adjacent fullerene molecules [4, 5]. The treatment of C₆₀ under variable conditions of high pressure and high temperature is leading to the production of three-dimensional polymeric phases of fullerite [6, 7], a first step to the synthesis of ultra hard fullerite phases [8]. Recently, Okada et al. [9] have predicted that the three-dimensionally polymerized fullerite might be formed by the application of uniaxial pressure to the two-dimensional polymeric tetragonal phase of C₆₀. According to their density-functional calculations, polymerization will take place at a lattice constant $c = 10.7 \text{ \AA}$, which is attainable at $P \approx 20.2 \text{ GPa}$. This polymerization will result in the formation of a stable metallic phase having 24 sp³ and 36 sp² hybridized C atoms in each C₆₀ molecule. To explore this prediction we have studied the pressure response of the two-dimensional tetragonal C₆₀ polymer at pressure up to 27.5 GPa by means of in-situ Raman measurements using the high-pressure diamond anvil cell (DAC) technique.

¹) e-mail: meletov@vergina.eng.auth.gr

Experiment The 99.99% pure pristine C_{60} powder material was subjected to pressures in the range of ≈ 2.5 GPa at a temperature of about 820 K to obtain 2D poly-crystalline C_{60} [10]. X-ray analysis, after the high-pressure treatment, confirmed that the crystal structure of the polymer is tetragonal (space group $I4mm$, $a = 9.082$ Å and $c = 14.990$ Å) [11].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectral width of the system was ≈ 4 cm^{-1} . The 514.5 nm line of an Ar^+ laser with beam power up to 45 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out using the DAC of Mao-Bell type [12]. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [13]. The phonon frequencies were calculated by fitting Voigt functions to the experimental Raman spectra.

Results and Discussion The Raman spectra of the C_{60} two-dimensional tetragonal polymer in the frequency region 200–2000 cm^{-1} and for various pressures are illustrated in Fig. 1. The initial Raman spectrum at 1.1 GPa is typical for this material and coincides with the earlier reported ones [14, 15]. It should be mentioned that the Raman spectra intensity distributions for various chips, taken from the same growth batch, are rather different. For the present study the optically uniform chips having the most intense Raman spectra were selected. The polymer spectrum is richer in structure than that of the pristine C_{60} due to the splitting of the Raman active degenerate modes or to the activation of silent modes caused by the lowering of symmetry. As the pressure increases the frequencies and the widths of the Raman bands gradually increase.

The most important changes in the Raman spectrum take place in the pressure region between 18 and 22 GPa. In the midpoint of this region the Raman spectrum of the material becomes very weak and structureless. At pressures above 22 GPa a new Raman spectrum appears which grows rapidly in intensity with increasing pressure up to 27.5 GPa, the highest pressure obtained in the present study. The Raman spectrum of the new phase differs sig-

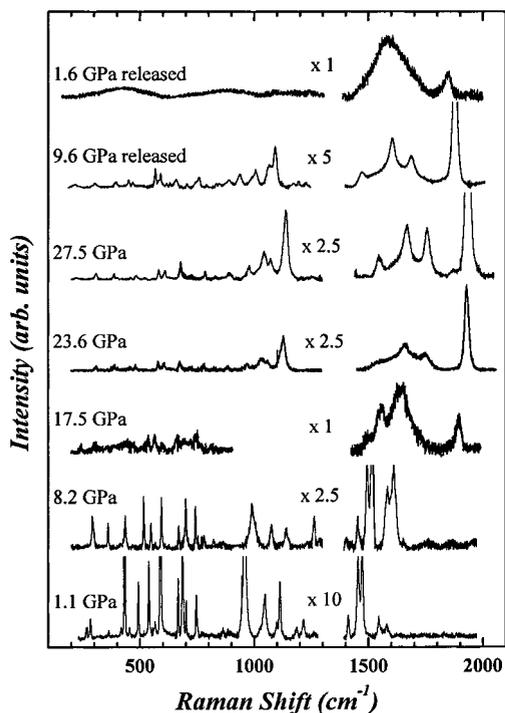


Fig. 1. Raman spectra of the 2D tetragonal C_{60} polymeric phase at room temperature for various pressures, recorded upon pressure increase and decrease

nificantly from the initial one in respect to the number of peaks, their intensities and positions. Despite the appearance of new very intense peaks the total number of Raman active modes in the high-pressure phase is almost one half of the corresponding number of modes in the initial one. The new peaks are located in the frequency region above 800 cm⁻¹, with the most intense of them located at a frequency of ≈1850 cm⁻¹. The peaks have mainly the same origin as in the case of the tetragonal C₆₀ polymer and may be related to the fullerene molecular cage. The decrease of pressure from 27.5 GPa down to 9 GPa does not lead to any changes in the Raman spectrum and the new phase remains stable under pressure release in this pressure region. As the pressure is released below 9 GPa, the spectrum loses most of its structure and contains two very weak and broad peaks, one at ≈420 cm⁻¹ and the other at ≈1580 cm⁻¹. This spectrum has similarities with the Raman spectrum of amorphous carbon. The narrow peak at ≈1840 cm⁻¹, which is retained in the spectrum down to a pressure of 1.6 GPa, is most likely related to a trace of the high pressure phase.

Figures 2 and 3 show the pressure dependence of the Raman active modes of the C₆₀ polymer for the pressure region investigated. The experimental data, shown by circles and squares, were obtained in two independent pressure runs. The open (solid) circles show the pressure dependence of the phonon frequencies under pressure increase (release) up to 12 GPa. The open (solid) squares are related with the second pressure run and show the pressure dependence of the same phonon modes under pressure increase (release) from ambient up to 27.5 GPa. The data obtained in the pressure region up to 12 GPa coincide, within experimental accuracy, for both pressure runs. The pressure dependence of the phonon modes, up to 12 GPa, does not show any anomaly and is reversible with pressure. On the contrary the pressure behavior of phonon

modes at pressures up to 27.5 GPa is not reversible and shows an anomaly around 20 ± 2 GPa (dashed area), where a number of new Raman peaks appear, while some of the old ones disappear. The dashed area 8.5 ± 0.5 GPa shows the pressure region where the sharp Raman peaks of the new phase disappear upon pressure release.

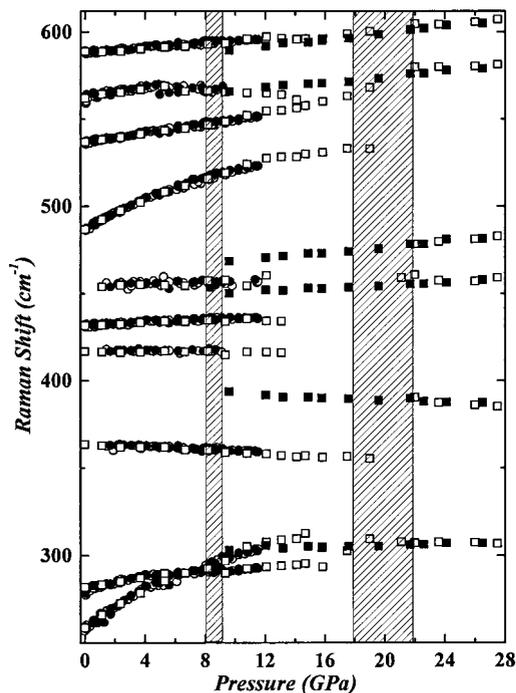


Fig. 2. Pressure dependence of the Raman modes of the tetragonal phase of the 2D C₆₀ polymer, in the frequency region 250–610 cm⁻¹. The open (solid) symbols denote data taken for increasing (decreasing) pressure; different symbols represent data from different experimental runs. The dashed areas around 8.5 ± 0.5 GPa and 20 ± 2 GPa denote the regions of material transformation

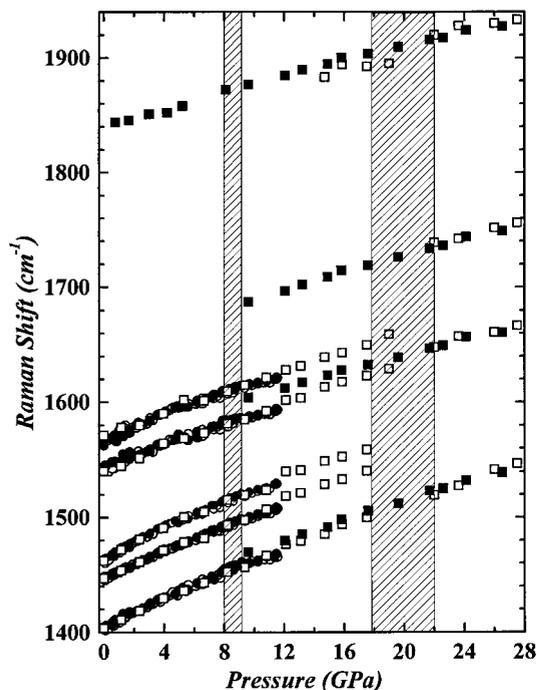


Fig. 3. Pressure dependence of the Raman modes of the tetragonal phase of the 2D C_{60} polymer in the frequency region $1400\text{--}1940\text{ cm}^{-1}$. The symbols have the same meaning as in Fig. 2

The obtained experimental data provide a strong indication that the material undergoes a phase transition at $\approx 20 \pm 2$ GPa. The gradual transformation of the initial prominent Raman spectrum to a diffuse one, followed by further transformation to a spectrum containing sharp peaks, may be related to the high-pressure induced three-dimensional polymerization of the material. The intermediate diffuse spectrum characterizes a disordered pre-transitional state of the material, when a number of double $C=C$ bonds of the fullerene molecule are destroyed due to the

random creation of the new polymeric bonds between adjacent molecules. The reduction of the total number of the Raman active modes in the high-pressure phase indicates a higher symmetry for the new phase. The appearance of the strong Raman modes in the new phase of C_{60} may be associated with some changes in the fullerene molecular cage and the creation of new out-of-plane polymeric network resulting in three-dimensional polymerization. Namely, the increased number of sp^3 hybridized carbon atoms per C_{60} molecule may result in an enhancement of the Raman mode similar to that of the diamond mode at 1332 cm^{-1} . We think that the Raman mode at 1150 cm^{-1} conforms to this case. The difference in frequencies may be associated with the increase of the sp^3 bond length from 1.54 \AA in diamond to 1.60 \AA in the three-dimensionally polymerized C_{60} [9]. Concerning the most intense Raman peak of the new phase at $\approx 1840\text{ cm}^{-1}$ it should be mentioned that this cannot be related to a fullerene molecular cage mode. Assuming that the high pressure phase involves a three-dimensional bonding, we may attribute this peak to the stretching vibration of the interfullerene bridging $C-C$ bonds, which are involved in the three-dimensional polymerization of the material [16].

Despite the theoretical prediction [9], the high-pressure phase is not stable and transforms to a new one under pressure release below 9 GPa. The Raman spectrum of the final phase has similarities with that of amorphous carbon. We assume that the final transformation may be associated with polymer destruction related to laser-induced overheating of the material. We also think that the detailed study of the new high-pressure phase, by means of other experimental methods is needed in order to shed light on the nature of this phase transition. In our opinion, the most important would

be an in-situ X-ray diffraction study of the phase transition in the 2D tetragonal polymer of C₆₀ at high pressure.

Acknowledgements The support by the General Secretariat for Research and Technology (GSRT), Greece, grant No. ΠΕΝΕΔ99, 99ΕΔ/62 is acknowledged. K.P.M. acknowledges the support by the GSRT, Greece, and the Russian Foundation for Fundamental Research, Russia, grant No. 99-02-17555. Authors thank Dr. A. Soldatov for rendering of the C₆₀ tetragonal 2D polymer, Mrs. I. Tsilika and Dr. S. Assimopoulos for assistance.

References

- [1] Y. IVASA, T. ARIMA, R. M. FLEMING et al., *Science*, **264**, 1570 (1994).
- [2] M. NUNEZ-REGUERO, L. MARQUES, J.-L. HODEAU et al., *Phys. Rev. Lett.* **74**, 278 (1995).
- [3] I. O. BASHKIN, V. I. RASHUPKIN, N. P. KOBEL'EV et al., *JETP Lett.* **59**, 258 (1994).
- [4] A. M. RAO et al., *Science* **259**, 955 (1993).
- [5] A. M. RAO, P. C. EKLUND, J.-L. HODEAU et al., *Phys. Rev. B* **55**, 4766 (1997).
- [6] V. V. BRAZKIN, A. G. LYAPIN, S. V. POPOVA et al., *Phys. Rev. B* **56**, 11465 (1997).
- [7] L. MARQUES et al., *Science* **283**, 1720 (1999).
- [8] V. D. BLANK, S. G. BUGA, N. R. SEREBRYANAYA et al., *Phys. Lett. A* **220**, 149 (1996).
- [9] S. OKADA, S. SAITO, and A. OSHIYAMA, *Phys. Rev. Lett.* **83**, 1986 (1999).
- [10] B. RENKER, H. SCHÖBER, R. HEID, and B. SUNDQVIST, in: *Molecular Nanostructures*, Eds. H. KUZMANY, J. FINK, M. MEHRING, and S. ROTH, World Scientific, Singapore 1998 (p. 322).
- [11] T. WÄGGER, A. SOLDATOV, B. SUNDQVIST et al., unpublished.
- [12] A. JAYARAMAN, *Rev. Sci. Instrum.* **57**, 1013 (1986).
- [13] D. BARNETT, S. BLOCK, and G. J. PIERMARINI, *Rev. Sci. Instrum.* **44**, 1 (1973).
- [14] J. ARVANITIDIS, K. P. MELETOV, K. PAPAGELIS, A. SOLDATOV, K. PRASSIDES, G. A. KOUROUKLIS, and S. VES, *phys. stat. sol. (b)* **215**, 443 (1999).
- [15] J. ARVANITIDIS, K. P. MELETOV, K. PAPAGELIS, A. SOLDATOV, K. PRASSIDES, G. A. KOUROUKLIS, and S. VES, *High Pressure Research* (in print).
- [16] D. A. LONG, *Raman Spectroscopy*, McGraw-Hill Publ. Co., London 1976 (p. 158).

