

PRESSURE RESPONSE OF THE HIGHER FULLERENE C₈₄ STUDIED BY RAMAN AND X-RAY SCATTERING

S. ASSIMOPOULOS^{a,*}, K. P. MELETOV^{a,b}, G. A. KOUROUKLIS^a, I. MARGIOLAKI^c,
S. MARGADONNA^c, K. PRASSIDES^{c,d}, T. J. S. DENNIS^e and H. SHINOHARA^e

^aPhysics Division, School of Technology, Aristotle University of Thessaloniki, GR-540 06 Thessaloniki, Greece; ^bInstitute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia; ^cSchool of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK; ^dInstitute of Materials Science, NCSR “Demokritos”, 153 10 Ag. Paraskevi, Athens, Greece; ^eDepartment of Chemistry, Nagoya University, Nagoya 464-8602, Japan

(Received 24 July 2001; In final form 17 September 2001)

The pressure behavior of the intramolecular phonon modes of the fullerene C₈₄ and its structural stability have been studied for the first time by means of Raman spectroscopy and synchrotron X-ray diffraction at high pressure up to ~10 GPa. The volume of the cubic unit cell has been measured as a function of pressure. The experimental data fitted by the Murnaghan equation-of-state (EOS) gave $K_0 = 19.5 \pm 0.9$ GPa and $K'_0 = 16.4 \pm 0.6$. The pressure coefficients and Grüneisen parameters of the intramolecular phonon modes of C₈₄ have been determined and compared with those of other fullerenes. The data obtained do not show any phase transition and the pressure behavior of the material is entirely reversible in the pressure region investigated.

Keywords: C₈₄; Fullerenes; High-pressure; Raman spectroscopy; X-ray scattering

1 INTRODUCTION

The higher fullerene C₈₄ is the third most abundant carbon cluster product from arc-processed graphite. The molecule of C₈₄ has a large number of isomers and ¹³C NMR studies indicated the highest yield for two isomers having symmetry D₂(IV) and D_{2d}(II) and respective 2:1 abundance ratio [1]. The successful separation of these two major isomers of C₈₄ [2] has intensified the studies of the physical properties of this material [3–6]. In this work we have studied, for the first time, the pressure behavior of the intramolecular phonon modes of the fullerene C₈₄ and its structural stability by means of Raman spectroscopy and synchrotron X-ray diffraction at high pressure. The pressure responses of the crystal lattice and of the phonon spectrum allow us to investigate the structural and chemical stability of the material and the role of intermolecular interaction upon pressure application.

* Corresponding author. Tel.: +3031995959; Fax: +30 31 995928; E-mail: assimop@vergina.eng.auth.gr

2 EXPERIMENT

The material under study was a mixture of the two major isomers $D_{2h}(\text{IV})$ and $D_{2d}(\text{II})$ of the C_{84} fullerene, with 2:1 abundance ratio. Separation of C_{84} was achieved by recycling HPLC using a Cosmosil 5PYE column and toluene as solvent. The crystalline samples for Raman and X-ray analysis, recrystallized from toluene with subsequent removal of residual solvent at $\sim 550\text{ K}$ under vacuum 10^{-5} Torr for 12 h and sublimed at $\sim 950\text{ K}$.

The 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 $\sim 5\text{ cm}^{-1}$. The 514.5 nm line of an Ar^+ laser was used for excitation. The laser power was kept lower than 5 mW , measured directly before the cell, in order to avoid the laser heating effects and related changes in the phonon spectrum [7]. Measurements of the Raman spectra at high pressure and room temperature were carried out using the diamond anvil cell (DAC) of Mao-Bell type [8]. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [9].

High-pressure X-ray diffraction experiments at ambient temperature were performed on beamline ID09 at the European Synchrotron Radiation Facility, Grenoble. The powder sample was loaded in a diamond anvil cell (DAC), which was used for the high pressure generation and was equipped with an aluminium gasket. The sample was introduced in a hole made in the gasket $70\text{ }\mu\text{m}$ deep and $200\text{ }\mu\text{m}$ in diameter. Silicone oil loaded in the DAC was used as a pressure-transmitting medium and the ruby fluorescence technique was used for pressure calibration. The diffraction patterns were collected using an image plate detector ($\lambda = 0.49953\text{ }\text{\AA}$). Masking of the strong Bragg reflections of the ruby chip and integration of the two-dimensional diffraction images were performed with the local ESRF FIT2D software. The data analysis was performed with the LeBail pattern decomposition technique.

3 RESULTS AND DISCUSSION

The Raman spectrum of C_{84} at normal conditions is shown in Figure 1. The spectrum is considerably richer than that of pristine C_{60} due to the lower symmetry of the C_{84} molecule as well as to the larger number of the Raman active modes. The Raman peaks are broadened with respect to those of the pristine C_{60} or C_{70} , which may be associated mainly with the fact that the sample is a two isomer mixture. The positions of the observed peaks are in agreement with those reported earlier for the pure isomers $D_{2h}(\text{IV})$ and $D_{2d}(\text{II})$ of the C_{84} fullerene molecule [5]. The pressure behavior of the most intense Raman modes was followed from the Raman spectra of C_{84} measured at pressure up to 10 GPa . The pressure dependence of the low energy Raman modes is shown in the inset of Figure 1. The open (closed) symbols represent the data for increasing (decreasing) pressure. Similar pressure dependence was also obtained for the rest of the Raman modes. No singularity is present and the spectra are entirely reversible under release of pressure. The characteristics of the pressure dependence of the Raman modes of the C_{84} are summarized in Table I, which includes the frequencies of a number of Raman peaks at normal conditions, their pressure coefficients as well as their Grüneisen parameters.

The pressure dependence of the volume of the cubic unit cell of the C_{84} mixture of isomers is shown in Figure 2 by solid cycles. The Rietveld refinements of the synchrotron X-ray powder diffraction profile at 20 K showed that the crystal structure of C_{84} is *fcc* (space group $Fm\bar{3}m$) with lattice constant $a = 15.817(4)\text{ }\text{\AA}$ ($15.924\text{ }\text{\AA}$ at $T = 300\text{ K}$) [2]. The solid line in

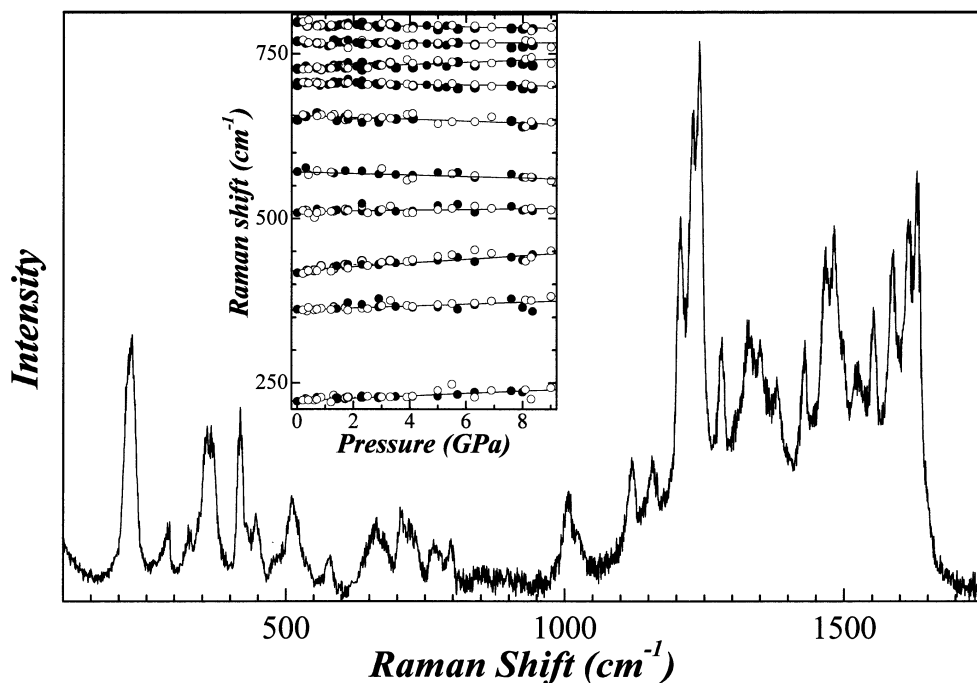


FIGURE 1 The Raman spectrum of the $D_{2(IV)}$ and $D_{2d(II)}$ isomer mixture of the C_{84} fullerene at ambient conditions. Inset: pressure dependence of the low energy intramolecular phonon modes of C_{84} for increasing (open symbols) and decreasing (closed symbols) pressure.

TABLE I Phonon Frequencies and Respective Pressure Coefficients for some of the C_{84} Raman Active Modes.

$\omega_i (P=0) (cm^{-1})$	$\partial\omega_i/\partial P (cm^{-1}/GPa)$	$\gamma_i = (K_0/\omega_i) \cdot (\partial\omega_i/\partial P)^\dagger$
222	1.7	0.149
363	1.1	0.059
420	2.8	0.130
512	-0.1	-0.004
576	-1.2	-0.041
659	-1.6	-0.047
706	-0.8	-0.022
727	1.3	0.035
768	-0.4	-0.010
796	-0.9	-0.022
1006	4.4	0.085
1025	3.8	0.072
1205	5.0	0.081
1227	4.0	0.064
1241	4.0	0.063
1429	5.6	0.076
1464	4.9	0.065
1483	5.2	0.068
1552	5.5	0.069
1586	4.2	0.052
1613	3.1	0.037
1630	3.2	0.038

[†] $K_0 = 19.5 \pm 0.9$ GPa obtained in this work.

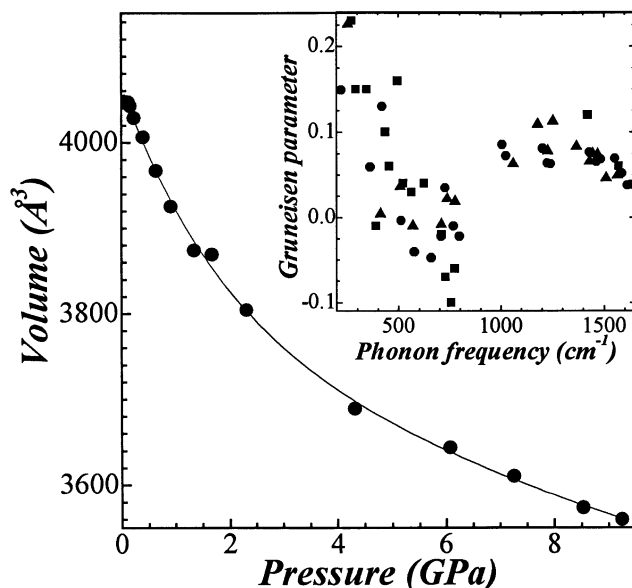


FIGURE 2 Experimental pressure dependence of the volume of the cubic unit cell of the $D_2(\text{IV})$ and $D_{2d}(\text{II})$ isomer mixture of C_{84} (closed circles) and a least-squares fit to the semiempirical second-order Murnaghan EOS (solid line). Inset: the Grüneisen parameters of the phonon modes of C_{84} , C_{70} and C_{60} (circles, triangles and squares, respectively).

Figure 2 is a least-squares fit of the ambient-temperature experimental data to the semiempirical second-order Murnaghan EOS:

$$P = \left(\frac{K_0}{K'_0} \right) \left[\left(\frac{V_0}{V} \right)^{K'_0} - 1 \right] \quad (1)$$

with $K_0 = 19.5 \pm 0.9$ GPa, $K'_0 = 16.4 \pm 0.6$, and $V_0 = 4064 \text{ \AA}^3$. As in the case of the Raman measurements, the X-ray study at high pressure does not show any phase transition or irreversible transformation of the material. In the inset of Figure 2 are shown the Grüneisen parameters of intramolecular phonon modes of C_{84} (solid circles), those of C_{60} (solid squares) and of C_{70} (solid triangles). The frequency dependence of the Grüneisen parameters for these three materials is very similar and has minor quantitative differences, which is consistent with their common origin.

In conclusion, the high pressure Raman and X-ray scattering study of the higher fullerene C_{84} do not show any phase transition or irreversible transformation of the material, which is stable in the pressure range up to 10 GPa.

Acknowledgements

The support by the General Secretariat for Research and Technology (GSRT), Greece, grant # ΠΕΝΕΔ99, 99ΕΔ/62 is acknowledged. K. P. M. acknowledges the support by the GSRT, Greece, and the Russian Foundation for Fundamental Research, Russia, grant # 99-02-17555. We thank the ESRF for provision of beamtime, NEDO for support under the Frontier Carbon Technology Program (KP) and JSPS for support under the Future Program for New Carbon Nanomaterials (HS).

References

- [1] Dennis, T. J. S., Kai, T., Tomiyama, K. and Shinohara, H. (1998). *Chem. Commun.*, 619.
- [2] Margadonna, S., Brown, C. M., Dennis, T. J. S., Lappas, A., Pattison, P., Prassides, K. and Shinohara, H. (1998). *Chem. Mater.*, **10**, 1742.
- [3] Kikuchi, K., Nakahara, N., Wakabayashi, T., Suzuki, S., Shinohara, H., Miyake, Y., Saito, K., Ikemoto, I., Kainosho, M. and Achiba, X. (1992). *Nature*, **357**, 141.
- [4] Dennis, T. J. S., Hulman, M., Kuzmany, H. and Shinohara, H. (2000). *J. Chem. Phys.*, **104**, 5411.
- [5] Krause, M., Hulman, M., Kuzmany, H., Kuran, P., Dunsch, L., Dennis, T. J. S., Inakuma, M. and Shinohara, H. (2000). *J. Mol. Struct.*, **521**, 325.
- [6] Hulman, M., Inakuma, M., Shinohara, H. and Kuzmany, H. (1999). *Synthetic Metals*, **103**, 2565.
- [7] Meletov, K. P., Liarokapis, E., Arvanitidis, J., *et al.* (1998). *Chem. Phys. Lett.*, **290**, 125.
- [8] Jayaraman, A. (1986). *Rev. Sci. Instrum.*, **57**, 1013.
- [9] Barnett, D., Block, S. and Piermarini, G. J. (1973). *Rev. Sci. Instrum.*, **44**, 1.