

phys. stat. sol. (b) **215**, 443 (1999)

Subject classification: 61.48.+c; 61.41.+e; 62.50.+p; 78.30.Na; 78.66.Tr; S5

Comparative Raman Study of the 1D and 2D Polymeric Phases of C₆₀ under Pressure

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(Received March 30, 1999)

The effect of symmetry lowering on the phonon spectra as well as the pressure effects on the vibrational spectrum of polymerized C₆₀ were studied by Raman spectroscopy. Drastic changes related to the splitting of degenerate modes of the C₆₀ molecule were observed together with selected softening of some of them. In spite of many similarities in the Raman spectra of the one- (1D) and two-dimensional (2D) polymeric forms of C₆₀, some salient differences in the peak intensities and the appearance of complementary modes are evident. In the Raman spectrum of the 2D polymer under high pressure, new modes, which may be related to the deformations of molecular cages, appear. The observed pressure effects are reversible and the material remains stable for pressures up to 8.8 GPa.

1. Introduction

C₆₀ has been found to polymerize both under illumination with visible or ultraviolet light [1] and upon alkali metal doping [2,3]. In addition, high pressure treatment of C₆₀ at high temperatures also leads to polymerization of the pristine material [4]. The polymerized forms of C₆₀ comprise of molecular units linked by bridging C–C covalent bonds [5]. The polymerization process involves either [2 + 2] cycloadditions between double bonds of neighboring C₆₀ molecules or the formation of single C–C bond linkages. The polymeric forms of C₆₀ have attracted considerable attention because of the variety of crystal structures and the interesting optical and mechanical properties [6].

The perturbations in the structure of the C₆₀ cages, caused by external disturbances like pressure, temperature, chemical bond formation etc., are manifested in the phonon spectrum. Thus, Raman spectroscopy, which probes inter- and intramolecular vibrations,

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is a suitable tool for the investigation of structure evolution and phase transitions in the polymeric modifications of C_{60} under pressure. In this work we present a detailed Raman study of the C_{60} two-dimensional (2D) polymer at high pressure and compare these results with the spectra of the one-dimensional (1D) and 2D polymeric phases at normal conditions.

2. Experiments

The samples used were prepared from sublimed 99.99% pure C_{60} powder pressurized in a piston and cylinder device. The pristine material was subjected to pressures in the range 1.1 to 1.2 GPa at temperatures 550 to 585 K and in the range 2.3 to 2.5 GPa at a temperature of about 820 K to obtain 1D and 2D polymerized C_{60} , respectively [5,7 to 11]. X-ray analysis of the samples from the same batch, after the high-pressure/high-temperature treatment, confirmed that the crystal structure of the 1D polymer is orthorhombic while the 2D polymer has a tetragonal structure [11].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a liquid-nitrogen cooled CCD detector system. The spectral width of the system was $\approx 5 \text{ cm}^{-1}$. The 514.5 nm line of an Ar^+ laser was used for excitation, with the laser power kept low enough in order to avoid depolymerization caused by laser heating effects and related changes in the phonon spectrum and the crystal structure [5,12]. Measurements of the Raman spectra at high pressures were carried out using the diamond anvil cell (DAC) of Mao-Bell type [13]. The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the well-known ruby fluorescence technique was used for pressure calibration [14].

3. Results and Discussion

The Raman spectra of the 1D and 2D polymers in the frequency region 100 to 2000 cm^{-1} at normal conditions are illustrated in Fig. 1. These data show that the 2D polymer is a better Raman scatterer than the 1D one. The phonon frequencies, as obtained by fitting the Raman data with Voigt lines, are tabulated in Table 1. The mode frequencies for the 1D polymer agree well with the corresponding data from Ref. [15] (Table 1). The lowering of the molecular symmetry caused by polymerization results in both the splitting of the Raman active H_g fivefold degenerate modes and the appearance of new peaks originating from initially inactive modes of the C_{60} molecule. The mode assignment in the polymeric fullerenes is rather uncertain due to overlapping of the split components. In Table 1 we follow the assignment given in Ref. [15], in which for simplicity the irreducible representations H_g and A_g of the C_{60} molecule are used for characterization of the appropriate modes of the polymer. The phonons marked by $\omega(1)$ to $\omega(7)$ are observed in this work.

The majority of the peaks in the two polymers have similar frequencies. The differences, associated with the intensity changes and the appearance of complementary modes, are the following:

- (i) For the 2D polymer, the split $H_g(1)$ mode component at 279 cm^{-1} is more intense than that at 257 cm^{-1} ; this behavior is reversed in the 1D polymer.
- (ii) For the 2D polymer, the relative intensities of the peaks at 432 and 950 cm^{-1} are higher than those for the 1D polymer.

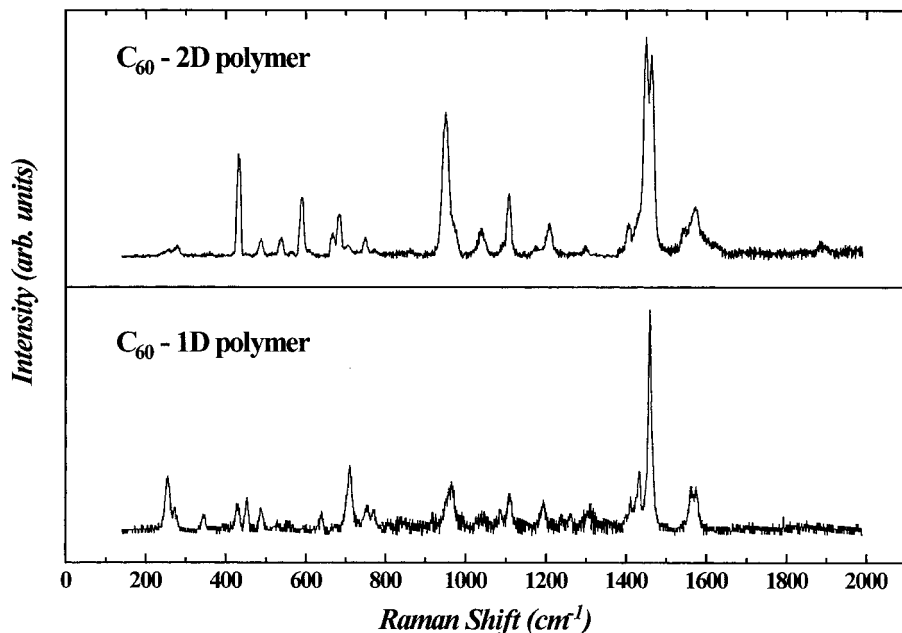


Fig. 1. Raman spectra of the C_{60} -polymers at ambient conditions

(iii) For the 1D polymer, the relative intensity of the peak at 710 cm^{-1} is higher than that in the 2D polymer.

(iv) The spectrum of the 1D polymer contains peaks at 345 , 453 and 639 cm^{-1} , which do not appear in the spectrum of the 2D polymer. It is important to note that the mode at 345 cm^{-1} observed in the Raman spectrum of high-pressure treated C_{60} has been proposed as a signature of the formation of linear chains of covalently bonded C_{60} molecules [15].

(v) The spectrum of the 2D polymer contains peaks at 589 , 610 , 666 , 684 , 1176 and 1888 cm^{-1} , which do not appear in the spectrum of the 1D polymer. The latter peak may arise from second order scattering related to the mode at 950 cm^{-1} , which is considerably stronger for the 2D polymer.

The most intense $A_g(2)$ pentagonal-pinch (PP) mode is downshifted for both polymers, as the formation of the intermolecular covalent bonds leads to a lower intramolecular average bond stiffness [6]. The fitting of Voigt line shapes to the Raman spectrum of the 1D polymer in the region of the PP mode gives two frequencies, 1458 and 1464 cm^{-1} , which are in excellent agreement with those observed in [5]. On the basis of Porezag's calculations [16], Sundqvist [6] suggested that the component at 1464 cm^{-1} might be due to the presence of C_{60} dimers, while that at 1458 cm^{-1} is the frequency of the PP mode in the case of C_{60} linear chains. In the 2D polymer the downshift of the PP mode might be even larger than that in the 1D polymer as additional intermolecular bonds are formed. We observe indeed two peaks with frequencies 1446 and 1464 cm^{-1} , in good agreement with recently reported data for the 2D tetragonal polymer [17]. The lower-energy component has been proposed to be the PP mode in the case of a 2D polymer [6]. However, from complementary analysis of Raman and infrared spectra of

Table 1

Frequencies of the intramolecular Raman modes of the 1D and 2D C₆₀ polymers. For comparison the mode frequencies of the 1D polymer taken from the literature are given

1D polymer ω (cm ⁻¹)	2D polymer ω (cm ⁻¹)	mode	1D ^{a)} polymer ω (cm ⁻¹)	1D polymer ω (cm ⁻¹)	2D polymer ω (cm ⁻¹)	mode	1D ^{a)} polymer ω (cm ⁻¹)
—	—	H _g (1) ^{a)}	249	967	972		967
255	257		256	1044	1039		1041
273	279		269, 275	1087	1090	H _g (5) ^{a)}	1087
345	—		344	1110	1108		1109
—	—	H _g (2) ^{a)}	416	—	1176		—
429	432		425, 431	1193	1208		1194
453	—		452	1239	—	H _g (6) ^{a)}	—
488	487	A _g (1) ^{a)}	489	1260	—		1261
528	537	ω (1)	—	1307	1299		1310
555	562	ω (2)	—	1398	—	H _g (7) ^{a)}	1398
—	589	ω (3)	—	1411	1405		1411
—	610	ω (4)	—	1426	1428		1426
639	—	H _g (3) ^{a)}	638	1433	—		1434
—	666		—	1448	—		1446
—	684		—	1458	1446	A _g (2) ^{a)}	1458
—	—		698	1464	1464		1464
710	706		708	—	1543	H _g (8) ^{a)}	—
748	753	H _g (4) ^{a)}	754	1562	—		1563
771	772		768, 775	1575	1571		1577
843	863	ω (5)	—	—	1599		—
917	—	ω (6)	—	—	1624		—
955	950		952	—	1888	ω (7)	—

^{a)} Data from Ref. [15].

the 2D tetragonal polymer of C₆₀ it was concluded that the presence of an appreciable amount of dimers in the system is unlikely [11]. This implies that the Raman mode at 1464 cm⁻¹ may be associated with a vibration, which is silent in the monomeric phase though becomes Raman active in 2D polymer.

Fig. 2 shows Raman spectra for the 2D polymer in the frequency region 200 to 800 cm⁻¹ under high hydrostatic pressure and room temperature together with the spectrum of the 1D polymer at ambient conditions for comparison. The vertical lines in Fig. 2 indicate the relatively strong peaks, which characterize each of the two polymers. For the 2D polymer these are the peaks with frequencies 589, 666 and 684 cm⁻¹, observed also by Davydov et al. [17] for a tetragonal (2D) polymer. These peaks were not observed in the Raman spectrum of the 1D orthorhombic polymer [15]. Consequently they may be used to characterize a 2D polymer.

The arrows indicate the new modes appearing at $P = 3.7$ GPa for the 2D polymer with frequencies 363, 417 and 457 cm⁻¹. It is obvious that the intensity for the peak at 363 cm⁻¹ increases considerably with pressure. At 8.8 GPa, two additional modes appear with frequencies of 753 and 782 cm⁻¹. Pressure application on the 2D polymer results in the intensity lowering of the mode at 432 cm⁻¹ and the increase of the two split components of the H_g(1) mode. The intensities of the Raman peaks of the 2D polymer under high pressure in the frequency range 200 to 550 cm⁻¹ become similar to

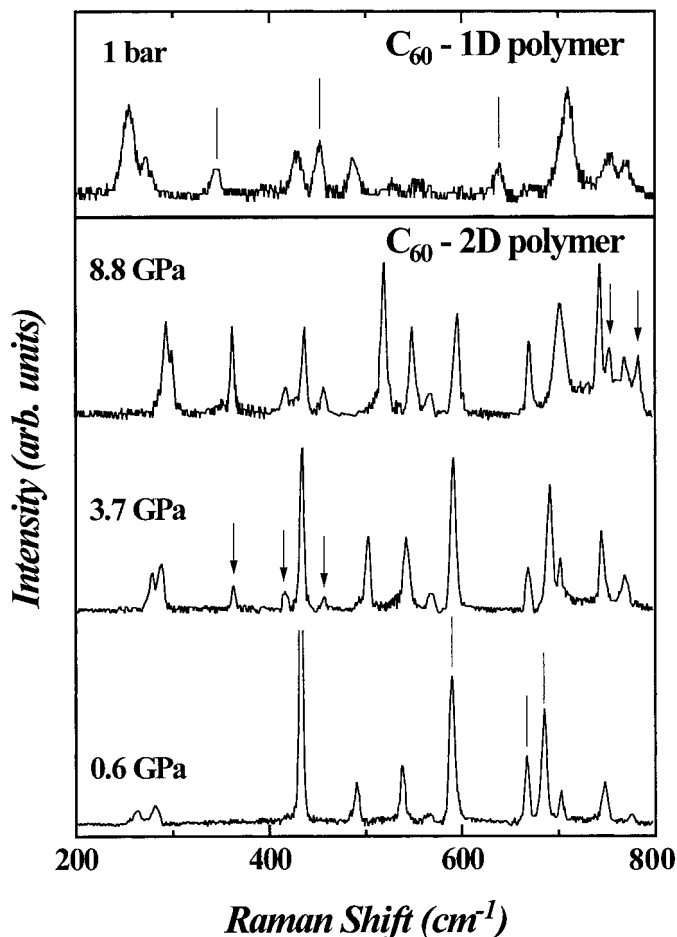


Fig. 2. Raman spectra of the 1D polymer at $P=1$ bar and the 2D polymer for various pressures up to 8.8 GPa at room temperature. The vertical lines indicate the different peaks for the two polymers, while the arrows denote the new modes which appear for the 2D polymer at high pressure

those of the 1D polymer. On the contrary, the spectrum of the 2D polymer above 550 cm^{-1} , including the frequency region near the PP mode, preserves its characteristics. All the above changes observed in the Raman spectrum of the 2D polymer under high pressure are reversible. This means that the intermolecular bonds are stable, at least for pressures up to 8.8 GPa, and the appearance of new modes cannot be related to polymeric bond breaking.

The two-dimensional polymeric C_{60} phase is anisotropic because of the different nature of the in-plane and out-of-plane intermolecular bonds. This implies that the compressibility of the 2D polymer is rather non-uniform up to some pressure limit, above which the material becomes more isotropic. The appearance of the new Raman modes in the spectrum of the 2D polymer may be connected with deformations of the C_{60} molecules under high pressure, as in the 1D polymer where the elongation of the molecules is responsible for the mode at 345 cm^{-1} .

Acknowledgements Support by NATO Grant (HTECH.CRG 97-2317) is gratefully acknowledged. K.P.M. acknowledges the support by the General Secretariat for Research and Technology, Greece, and the Russian Foundation for Fundamental Research (Grant No. 99-02-17555). A.S. acknowledges the Royal Society/NATO fellowship.

References

- [1] A.M. RAO, P. ZHOU, K.-A. WANG et al., *Science* **259**, 955 (1993).
- [2] P.W. STEPHENS, G. BORTEL, G. FAIGEL et al., *Nature* **370**, 636 (1994).
- [3] K. PRASSIDES, K. VAVEKIS, K. KORDATOS et al., *J. Amer. Chem. Soc.* **119**, 834 (1997).
- [4] Y. IWASA, T. ARIMA, R.M. FLEMING et al., *Science* **264**, 1570 (1994).
- [5] P.-A. PERSSON, U. EDLUND, P. JACOBSSON et al., *Chem. Phys. Lett.* **258**, 540 (1996).
- [6] B. SUNDQVIST, *Adv. Phys.* **48**, 1 (1999).
- [7] R. MORET, P. LAUNOIS, P.-A. PERSSON, and B. SUNDQVIST, *Europhys. Lett.* **40**, 55 (1997).
- [8] A. SOLDATOV, O. ANDERSSON, B. SUNDQVIST, and K. PRASSIDES, *Mol. Mater.* **11**, 1 (1998).
- [9] Å. BARTHOLDSON, S. FREDRIKSSON, and B. SUNDQVIST, unpublished.
- [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 Publ. Co., Singapore 1998 (p. 322).
- [11] T. WÄGBERG, A. SOLDATOV, B. SUNDQVIST et al., unpublished.
- [12] K.P. MELETOV, E. LIAROKAPIS, J. ARVANITIDIS et al., *Chem. Phys. Lett.* **290**, 125 (1998).
- [13] A. JAYARAMAN, *Rev. Sci. Instrum.* **57**, 1013 (1986).
- [14] D. BARNETT, S. BLOCK, and G.J. PIERMARINI, *Rev. Sci. Instrum.* **44**, 1 (1973).
- [15] J. WINTER, H. KUZMANY, A. SOLDATOV et al., *Phys. Rev. B* **54**, 17486 (1996).
- [16] D. POREZAG, M.R. PEDERSSON, T. FRAUENHEIM, and T. KOHLER, *Phys. Rev. B* **52**, 14963 (1995).
- [17] V.A. DAVYDOV, L.S. KASHEVAROVA, A.V. RAKHMANINA et al., *Phys. Rev. B* **58**, 14786 (1998).