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High-pressure-induced metastable phase in tetragonal 2D polymeric C_{60}

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Abstract

The structural stability of the tetragonal two-dimensional (2D) polymeric phase of C_{60} has been studied under pressure up to ~24 GPa and room temperature by means of in situ Raman scattering. An irreversible transformation of the material to a new phase was observed at pressure ~20 GPa. The phonon spectrum of the high-pressure phase provides a strong indication that the fullerene molecular cage is retained and therefore this phase may be related to a three-dimensional (3D) network of C_{60} cages. The new phase remains stable upon slow release of pressure to ambient conditions. The recovered material is metastable and transforms in air by detonation under laser irradiation to partially dimerized C_{60}. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The polymerization of pristine C_{60} under high-pressure and high-temperature conditions results in the formation of fullerene cage networks of various dimensionalities [1–4]. The covalent polymeric bonds are usually formed by the so-called $[2+2]$ cyclo-addition mechanism via the formation of four-membered rings between adjacent fullerene molecules [5]. The crystal structures of the polymeric phases have been identified as one-dimensional (1D) orthorhombic [2], two-dimensional (2D) tetragonal [2], 2D rhombohedral [1,2] and three-dimensional (3D) face-centered cubic [3]. In addition, the treatment of fullerite under highly non-uniform pressure and high temperature leads to the production of several disordered polymeric phases, the so-called super- and ultra-hard fullerite phases [6]. Detailed studies [7,8] performed recently on these phases have revealed their crystal structure confirming their 3D polymeric character.

Three-dimensional polymers of C_{60} are characterized by a large number of intermolecular covalent bonds formed by sp^3 like fourfold coordinated carbon–carbon bonds. Theoretical studies by Okada et al. [9] have predicted that three-dimensionally polymerized fullerite might be formed by the application of uniaxial pressure to the 2D

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polymeric tetragonal phase of C_{60}. According to their density-functional calculations, polymerization will take place at a lattice constant $c = 10.7$ Å, which is attainable at a pressure of ~20.2 GPa. This polymerization will result in the formation of a stable metallic phase having 24 sp^3 and 36 sp^2 hybridized C atoms in each C_{60} molecule. Another theoretical study, by Burgos et al. [10], predicts that uniaxial compression perpendicularly to the chains in 1D or to the planes in 2D polymerized C_{60} materials leads to a 3D polymerization of C_{60} with 52, 56 and even 60 sp^3 coordinated carbon atoms per fullerene molecule. These transformations are expected at a pressure lower than 14 GPa and the new phases, having large bulk and shear moduli, should be semiconductors with gaps larger than 2 eV.

To explore the above theoretical predictions we have studied the pressure response of the 2D tetragonal C_{60} polymeric phase at pressure up to ~24 GPa by means of in situ Raman spectroscopy using the diamond anvil cell (DAC) technique. Our interest has been focused on the experimental study of the pressure-induced transformations of the 2D tetragonal polymeric phase and the structural stability of the high-pressure polymeric phases.

2. Experimental

The 2D polymerized C_{60} was obtained by subjecting 99.99% pure C_{60} powder to a pressure of 2.2 GPa at a temperature of about 820 K [11]. After treatment, a Raman analysis showed the very characteristic spectrum of tetragonal C_{60} [11,12] with no detectable indications of orthorhombic or rhombohedral phases. Although this phase is usually considered to have the space group *Immm*, a recent single-crystal study has shown that the symmetry is actually $P4_2/mmc$ [12]. However, the difference is small and not easily detectable with powder X-ray diffraction.

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectra were taken in the backscattering geometry by the use of a micro-Raman system comprising an OLYMPUS microscope equipped with objectives with magnification 100× and 20× and spatial resolution of ~1.7 and ~8 μm, respectively. The spectral width of the system was ~4 cm^{-1}. The 514.5 nm line of an Ar^+ laser with beam power below 20 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out using a DAC of Mao–Bell type [13]. The 4:1 methanol–ethanol mixture was used as pressure-transmitting medium and the ruby fluorescence technique was used for pressure calibration [14].

The samples used in the present studies had dimensions of ~100 μm and were selected from the batch material for their intense, clear and spatially uniform Raman response, typical for 2D polymeric tetragonal phase.

3. Results and discussion

Raman spectra of the C_{60} 2D tetragonal polymeric phase, in the frequency region 120–2000 cm^{-1} and for several pressures up to 24.1 GPa, are shown in Fig. 1. The initial spectrum taken at ambient conditions represents a typical Raman spectrum of this material and is identical with the spectra reported earlier [12,15,16]. This spectrum is richer in structure than that of pristine C_{60} due to the splitting of the Raman active fivefold degenerate (H_g) phonon modes and/or to the activation of silent modes. As the pressure increases the Raman peaks shift to higher energies and their bandwidths gradually increase. The broadening of the Raman peaks is further enhanced for pressures higher than 10 GPa, most probably due to the solidification of the pressure-transmitting medium. At the same time the background in the high-energy region of the spectrum is gradually enhanced and for pressures higher than 15 GPa is extended to the low-energy region of the spectrum. As the fluorescence from the sample is appearing in another energy region, this background may be attributed to the enhancement of strain and inhomogeneity within the sample induced at higher pressure. Dramatic changes in the Raman spectrum are first recorded at the pressure of 20.7 GPa. New features appear which rapidly grow in

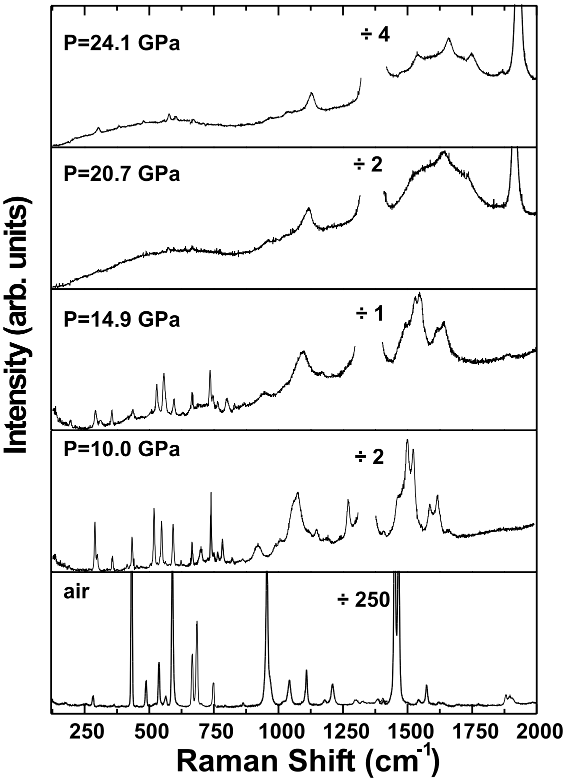

Fig. 1. Raman spectra of the 2D tetragonal C_{60} polymeric phase at room temperature for various pressures, recorded upon pressure increase. Note that the spectral region of the strong first-order Raman peak of diamond (~1330 cm^{-1}) is excluded.

intensity with increasing pressure up to the highest pressure attained in the present study. The new Raman spectrum differs significantly from the initial one with 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 final spectrum is considerably smaller than the number of modes observed in the spectrum of the initial phase. The new peaks are located in the frequency region above 1000 cm^{-1}, with the most intense of them recorded at a frequency of ~1920 cm^{-1}. A number of less intense peaks are located in the frequency region below 1000 cm^{-1}. The majority of the peaks can be tracked back to the peaks observed in the tetragonal C_{60} polymeric phase and may be related to the fullerene molecular cage. Nevertheless, some of the peaks, located in the high-energy region, do not have any obvious relation with fullerene molecular cage modes and therefore should be of a different origin.

Fig. 2 shows the Raman spectra of the material upon pressure release. The decrease of pressure, ~24 GPa down to ambient conditions, results in a gradual shift of the Raman peaks to lower energies. The release of pressure does not lead to any observable changes in the Raman intensity distribution and the high-pressure phase remains stable down to ambient pressure. The bottom spectrum in Fig. 2 was recorded at normal conditions with the sample being exposed to air after disassembling the DAC. The Raman spectrum of the high-pressure phase at ambient conditions is quite

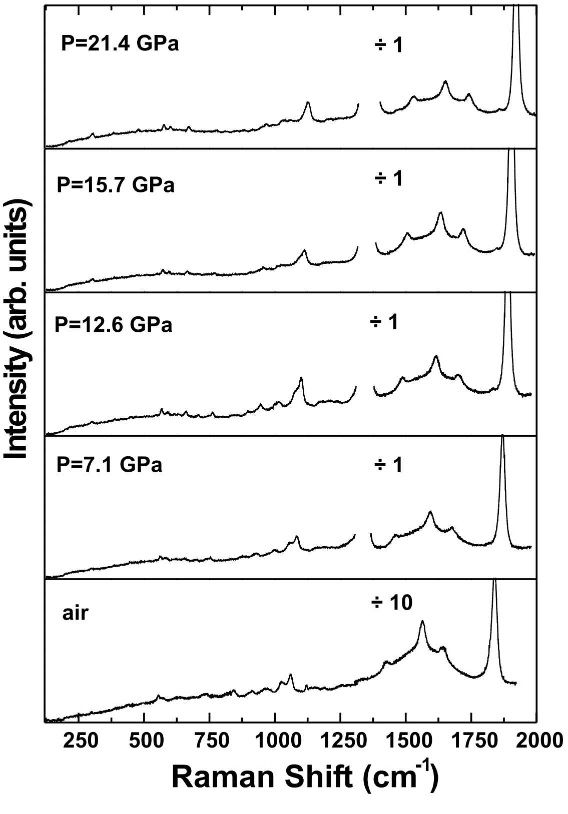

Fig. 2. Raman spectra of the high-pressure phase of the 2D tetragonal C_{60} polymer at room temperature for various pressures, recorded upon pressure decrease. Note that the spectral region of the strong first-order Raman peak of diamond (~1330 cm^{-1}) is excluded.

different from that of the initial 2D tetragonal polymeric phase of C_{60}. The Raman peak positions for the initial 2D tetragonal polymeric phase of C_{60} and those of the recovered high-pressure phase, at ambient conditions, are shown in the first two columns of Table 1.

The recovered sample was tested by means of micro-Raman probing at various sites in order to

Table 1
Phonon frequencies and relative intensities observed in tetragonal 2D polymeric C_{60}, high-pressure phase and the recovered phases

A/A	Tetragonal 2D polymeric C_{60}		High-pressure phase		Pristine/dimerized/C_{60}		Diamond-like carbon phase	
	Frequency (cm^{-1})	Intensity[a]	Frequency (cm^{-1})	Intensity[a]	Frequency (cm^{-1})	Intensity[a]	Frequency (cm^{-1})	Intensity[a]
1	124.3	vw						
2	176.2	vw	164.6	w				
			208.7	w				
3	238.6	vw	243.6	w				
4	255.3	vw			266.1	vw		
5	282.2	w	299	w				
6	309.1	vw						
7	362.6	vw	389.8	w				
8	431.7	vs	437.6	w	427.4	vw		
9	487.4	m			488.7	vw		
10	537.6	s			522.6	vw		
11	562.7	w	556.2	m				
12	589.1	vs	622.5	w				
13	666	s						
14	684.5	s	687.5	vw	703.8	vw		
15	748	m	722.8	w	747.2	vw		
			736.9	w				
16	793.5	vw	767.1	vw	767.6	vw		
			817.8	vw				
17	863.5	w	842.4	vw	846.8	vw		
			899.8	vw				
18	955.4	vs	963.5	w	956.3	vw		
19	1019.5	vw	1026.7	m				
20	1042.3	m	1059.5	m				
21	1108.8	m						
22	1179.1	w	1188	vw				
23	1209.5	w			1238.9	vw		
24	1299.2	vw	1251.8	vw				
25	1326.2	vw			1327.8	vw	1342	s
26	1384.5	w						
27	1406	w	1424.7	m	1420	m		
28	1450.1	vs			1460	m		
29	1465.1	vs			1464.4	s		
30	1543.6	w						
31	1573.8	m	1564.1	s	1566.5	m	1591.3	m
32	1620.1	vw						
33	1637.7	vw	1642.9	s				
34	1695.2	vw						
35	1774.6	vw						
36	1880.3	w	1842	vs				
37	1895.1	w						

[a] Intensity characterization: very weak (vw), weak (w), medium (m), strong (s), and very strong (vs).

check the uniformity of its Raman response. A very strong and sharp peak at 1840 $\mathrm{cm^{-1}}$, a number of associated weaker peaks in its vicinity and a relatively small background characterize the Raman spectra, recorded from several sites of the sample. According to the results of the micro-Raman probing, the typical dimensions of these sites do not exceed ~10 μm. In the neighboring regions, the Raman peak at 1840 $\mathrm{cm^{-1}}$ is broadened and its intensity decreases further away from these sites in proportion to the distance. At the same time the background is enhanced obscuring the fine structure of the spectrum in the low-energy region. Our observations from several runs indicate that, after the phase transition, there can be found between 3 and 5 sites related to the high-pressure phase and characterized by well-resolved Raman spectra. Finally, it is very important to note that the recovered sample was in fact in a metastable phase which was detonated upon laser irradiation with intensity ~0.35 mW at 514.5 nm. Note that the laser power density on the sample, under these conditions, is bigger than the density reaching the sample inside the high-pressure cell due to the different optical systems used (different magnification factors) and also the thermal conditions (thermal conductivity) are different in the two cases, as the sample in the cell is surrounded by the pressure-transmitting medium. The detonation is a rapid 'explosive' process, which was probably initiated by the thermal energy deposited by the probing laser beam and resulted in the rapid relaxation of the built-in strain in the sample. This process has always taken place after a time period of a few days from the moment of the exposure of the recovered sample to air and at the present time it is very difficult to make any statement concerning the stability of the high-pressure phase with respect to time or to laser power density under the present experimental conditions.

The results of the micro-Raman probing of the recovered sample at ambient conditions before and after detonation are presented in Fig. 3, along with the spectrum of the initial 2D phase (a) which is included for comparison. The spectrum in (b) was taken before the sample detonation and is that of the high-pressure phase. The two lower spectra in Fig. 3c,d taken by means of micro-Raman probing from several pieces, resulting from the detonated sample, are related to 'diamond-like' graphite and to a mixture of pristine (molecular) and dimerized C_{60} phases. The main part of the detonated sample is related to the pristine or partially dimerized C_{60} phase as evident from its Raman spectrum (Fig. 3d). The diamond-like graphite, which is only a small part of the detonated sample, has a strong Raman peak at 1342 $\mathrm{cm^{-1}}$ resembling the 1332.5 $\mathrm{cm^{-1}}$ peak of the diamond (Fig. 3c). The second Raman peak of this phase, at 1591 $\mathrm{cm^{-1}}$, is similar to that of the 1580 $\mathrm{cm^{-1}}$ peak of graphite. This diamond-like phase was not present in the starting material. We have recorded the spectrum of this phase after the detonation but we are not

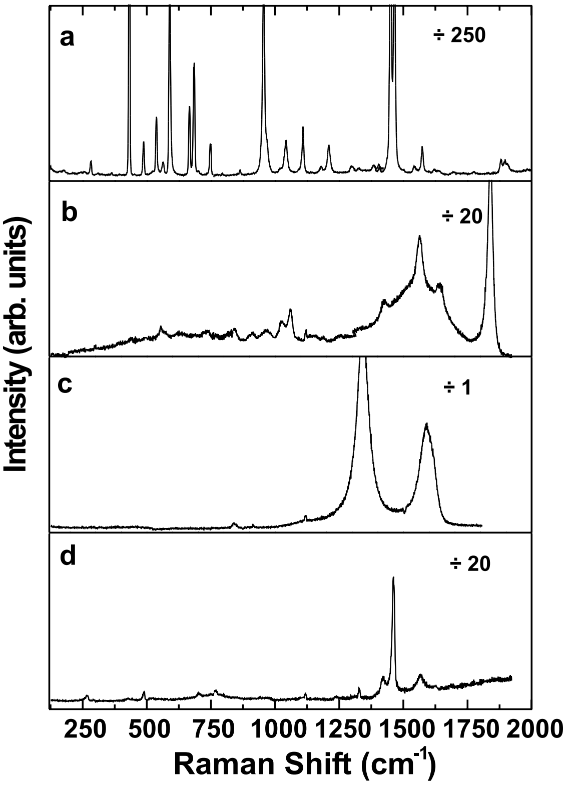

Fig. 3. Raman spectra of the initial 2D tetragonal polymeric phase of C_{60} and of the recovered sample recorded at ambient conditions by means of micro-Raman probing: (a) the initial 2D tetragonal polymeric phase; (b) the high-pressure phase of the 2D tetragonal C_{60} polymer; (c) the diamond-like graphite phase identified among the pieces of the detonated sample; (d) the pristine/dimerized C_{60} phase identified as the main component among the pieces of the detonated sample.

sure if this phase was present in the recovered sample before its detonation. The Raman peak positions observed in these two phases at ambient conditions are also tabulated in Table 1. Fullerite phases having Raman spectra similar to those in Fig. 3c have been observed earlier in C_{60} treated at a pressure of 12.5 GPa and a temperature of 900°C [17] or a pressure of 9.5 GPa and a temperature of 1500°C [18]. These phases were characterized by X-ray and micro-hardness studies as disordered carbon phases having high density and hardness [17,18].

Our experimental data provide a strong indication that the material undergoes a phase transition at $\sim$20 GPa. The irreversible transformation of the initial prominent Raman spectrum to a new well-resolved one took place via an intermediate rather diffuse Raman spectrum, which characterizes a disordered pre-transitional state of the material. This intermediate phase was present in a pressure range of $\sim$2 GPa. The retention of the phonon modes of the C_{60} cage in the new phase and the specific pre-transitional behavior are indications that the high-pressure phase may be related to a 3D polymerization, which is not exactly a phase transformation but a solid state chemical reaction. Another argument in favor of the 3D polymerization is the reduction of the total number of Raman active modes in the high-pressure phase, which agrees well with an expected higher symmetry for the 3D polymeric phase. Note also that the Raman peak at 1042 cm^{-1}, which is associated with covalent intermolecular bonds in tetragonal 2D polymerized C_{60} [19], is split into two broad components with frequencies 1026 and 1060 cm^{-1} in the high-pressure phase. We suggest that this may be explained assuming that the high-pressure phase possesses at least two types of fourfold coordinated sp^3-like hybridized carbon atoms, which form in-plane (2D) and out-of-plane (3D) intermolecular bonds with different bond lengths. The frequencies of this band have been observed to differ significantly between different polymeric phases, such as orthorhombic and tetragonal C_{60} [11], and a double-peak structure is often observed in spectra from mixed phases.

Concerning the most intense Raman peak of the high-pressure phase at $\sim$1840 cm^{-1}, it should be noted that this cannot be related to any mode in the fullerene molecular cage. Its appearance may be associated with a considerable distortion of the pentagonal-pinch mode of the pristine C_{60} due to the breakdown of a large number of double C=C bonds and sp^3 hybridization of the carbon atoms involved in the intermolecular bonding in the high-pressure phase. A strong Raman peak at 1840 cm^{-1} in some chemical compounds of carbon is related to the stretching vibration of an isolated double C=C bond [20]. The existence of this mode in the high-pressure phase is not compatible with the model for 3D polymerization proposed in Ref. [10], and the molecular dynamics calculations for the 3D polymeric phases [10] do not predict any phonon mode in the frequency region above 1600 cm^{-1}. Our experimental results on the transition pressure ($\sim$20 GPa) agree well with the theoretical predictions of Okada et al. [9] and are in disagreement with Burgos et al. [10] who predict a value of $\sim$14 GPa.

Despite the optical homogeneity of the samples used in the present study, the transformed material is always inhomogeneous and contains both the new high-pressure phase and disordered carbon phases. Taking into account the polycrystalline nature of the initial 2D polymeric samples we suppose that, under the present experimental conditions, the transformation to the well-ordered high-pressure phase may be possible only for a few small single-crystal grains of the material, whose crystallographic *c*-axes have accidentally been oriented in the preferred direction for the transition. This is related with the assumed uniaxial compression perpendicular to the planes of the 2D polymer in the theoretical studies [9,10]. From the experimental point of view the solidification of the pressure-transmitting medium at $P \geqslant 10$ GPa leads to the change from the hydrostatic compression to quasi-hydrostatic with significant uniaxial components.

Finally, we think that a 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 desirable would be an in situ X-ray diffraction study under pressure or an X-ray diffraction of the recovered sample.

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