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Pressure-induced transformation and phonon modes of the two-dimensional rhombohedral polymer of C_{60}: A Raman spectroscopic study

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The Raman spectra and stability of the two-dimensional rhombohedral (2D-R) polymeric phase of C_{60} have been studied as a function of pressure up to ~30 GPa at room temperature. The pressure dependence of the phonon frequencies is rather smooth and reversible to $P \leqslant 15$ GPa. At higher pressure the initially sharp and distinct Raman peaks become very broad and diffuse and the material undergoes an irreversible transformation to a new rather disordered phase. The intensity of the $A_g(2)$ pentagonal pinch (PP) mode rapidly decreases in the pretransitional pressure range and vanishes in the new phase. The high-pressure phase is recovered at normal conditions but is metastable and transforms under heating to a mixture of pristine and dimerized C_{60} as was evident by their Raman spectrum. The quenching of the PP mode, the retention of the molecular cage, and the irreversibility of the transition are the indications that the new high-pressure phase may be formed by random covalent bonding between C_{60} molecular cages in adjacent polymeric sheets of the 2D-R polymer of C_{60}.

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I. INTRODUCTION

Polymerization of C_{60} results in considerable changes to the crystal structure, electron and phonon spectra, and stability of the pristine fullerene material.[1] The existence of 30 double C=C bonds in the molecular cage allows for the formation of a variety of polymeric phases of C_{60}. The C_{60} has been found to polymerize under light illumination[2] as well as upon alkali-metal doping.[3] The covalent polymeric bonds are usually formed by the so-called [2+2] cycloaddition reaction via the formation of four-member rings between adjacent fullerene molecules.[2] However, the most effective way to polymerize C_{60} is by treatment of the material under various conditions of high pressure and high temperature (HPHT).[4] The crystal structure of the C_{60} polymers depends strongly on the pressure and temperature treatment conditions. Thus, the C_{60} molecules form linear polymeric chains having a one-dimensional orthorhombic (1D-O) crystal structure and/or dimers at lower pressure and temperature. Planar polymeric sheets with either a two-dimensional rhombohedral (2D-R) or a two-dimensional tetragonal (2D-T) crystal structure are formed at intermediate pressure and temperature.[4,5] A face-centered-cubic structure based on three-dimensionally cross-linked polymerization of the material was obtained under HPHT treatment at higher pressure and temperature.[6] In addition, the treatment of the pristine material under high nonuniform pressure and high temperature leads to the formation of several disordered polymeric phases, the so-called ultrahard fullerite phases, which have three-dimensionally cross-linked polymeric bonding.[7–9]

The polymerization of C_{60} is associated with the destruction of a number of double C=C bonds in the molecular cage and the creation of intermolecular covalent bonds by sp^3-like fourfold coordinated carbon atoms. Their number increases from 4 to 8 and to 12 per molecular cage for 1D-O, 2D-T, and 2D-R polymeric phases, respectively, and it is expected to increase further in the three-dimensional (3D) polymeric phases. Theoretical studies[10,11] have predicted that the 3D polymerization might occur upon application of uniaxial pressure perpendicular to the polymeric chains (sheets) of the linear (planar) polymers of C_{60}. According to density-functional calculations,[10] the planar 2D-T polymer may transform to an ordered 3D-polymeric phase via the formation of covalent bonds between molecules in adjacent polymeric sheets at a lattice constant $c = 10.7$ Å, which is attainable at a pressure of ~20.2 GPa. As a result, a stable metallic phase with 24 sp^3-like and 36 sp^2-like hybridized carbon atoms per C_{60} molecule may be obtained. Numerical calculations[11] predicted that uniaxial compression of linear and planar polymers of C_{60} leads to 3D polymerization with 52, 56, and even 60 sp^3-like coordinated carbon atoms per C_{60} molecular cage. These transformations are expected to take place at pressures lower than 14 GPa and the new phases are semiconducting with large bulk and shear moduli.

The phonon spectra of the various fullerene-related materials are very sensitive to any distortion of the molecular cage, induced by external perturbations, such as pressure or chemical bond formation.[12,13] The Raman and infrared spectra of polymeric fullerenes are very prominent and differ significantly among the 1D-O, 2D-R, and 2D-T phases as has been shown by detailed studies of their optical spectra combined with x-ray structural investigations.[14] Thus, Raman spectroscopy can be used reliably for the identification of the various polymeric phases of C_{60} as well as for the *in situ* studies of their stability at high pressure. Raman studies of the 2D-T polymeric phase of C_{60} at high pressure have revealed irreversible changes in the Raman spectra of this material near 20 GPa,[15,16] which have been attributed to its further polymerization. These experimental findings are consistent with the theoretical predictions of Okada *et al.*[10] On the other hand, a high-pressure x-ray study of the 2D-T polymer has shown that the material undergoes an irreversible amorphization in the pressure region between 10 and 20 GPa.[17] A recent Raman study of the 2D-R polymer of C_{60} has also revealed an irreversible transformation to a disordered high-pressure phase at ~15 GPa characterized by very diffuse Raman bands.[18]

In the present paper we report a detailed *in situ* study of the Raman spectra of the 2D-R polymeric phase of C_{60} at pressure up to ~30 GPa using the diamond-anvil cell technique. Our study is especially focused on the pressure behavior of the intramolecular phonon modes and the structural stability of the 2D-R polymer at high pressure. The pressure dependence of the Raman frequencies is rather smooth and reversible with pressure up to 15 GPa. At higher pressure, the 2D-R polymer transforms irreversibly to a new phase characterized by very diffuse Raman bands related to a highly disordered state. This phase is stable upon further increase of pressure up to 30 GPa and remains stable during the release of pressure down to ambient conditions. The recovered high-pressure phase of the 2D-R polymer is metastable at normal conditions and transforms to a mixture of C_{60} monomers and dimers upon heating to ~600 K.

II. EXPERIMENT

The 2D-R polymer of C_{60} was obtained by subjecting powder of pristine C_{60} with purity of 99.99% to a pressure of $P \approx 5$ GPa at a temperature of 773 K. The x-ray analysis, after the high-pressure treatment, confirmed that the crystal structure of the polymer is rhombohedral (space group $R\overline{3}m$; $a = 9.22$ Å and $c = 24.6$ Å).[4] A recent single-crystal study,[19] along with a more accurate determination of the structural parameters, have revealed a very interesting aspect concerning the stacking sequence of the polymeric layers. Namely, taking into account the C_{60} cage positions, we may have a structure with an ABCABC stacking sequence,[5] or another one with a ACBACB stacking sequence.[19] These two stacking sequences are not equivalent, differing in the cage orientations and therefore in the conducting cage faces (hexagonal or pentagonal) between the polymeric layers. Packing energy calculations[20] predict that the ACBACB stacking sequence would have produced the most stable structure in accordance with the single-crystal studies.[19] The samples used for the high-pressure measurements had dimensions of ~100 μm and have been selected from the batch material by means of micro-Raman probing for their intense, clear, and spatially uniform Raman response, typical of the 2D-R polymeric phase.[14]

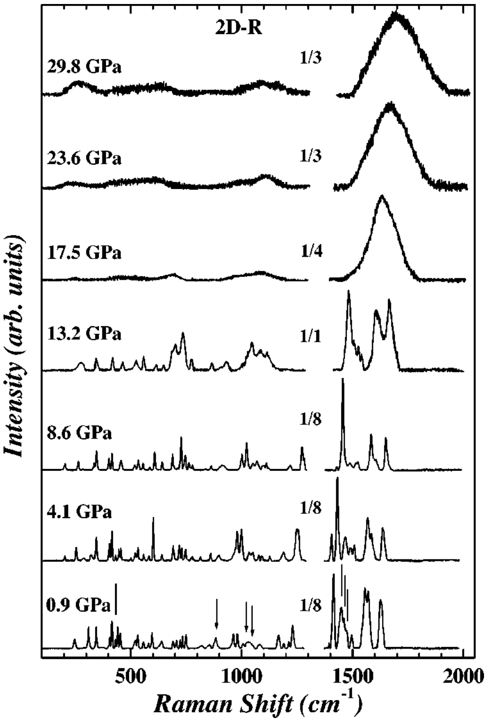

FIG. 1. Raman spectra of the 2D-R polymeric phase of C_{60} at room temperature and various pressures, recorded upon pressure increase. The vertical lines indicate peaks related to the presence of oligomers in the material, while the vertical arrows indicate methanol-ethanol mixture peaks.

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a liquid-nitrogen-cooled charge-coupled device detector system. The spectra were taken in the backscattering geometry with the use of a micro-Raman system comprising an OLYMPUS microscope equipped with an objective of 20 times magnification and a spatial resolution of ~8 μm. The spectral width of the system was ~4 cm^{-1}. The 514.5 nm line of an Ar^+ laser with beam power below 10 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out in a number of pressure runs using a diamond-anvil cell of the Mao-Bell type.[21] The 4:1 methanol-ethanol mixture was used as the pressure-transmitting medium and the ruby fluorescence technique was used for pressure calibration.[22]

III. RESULTS

The Raman spectra of the 2D-R polymeric phase of C_{60}, in the frequency region 100–2000 cm^{-1} and for various pressures up to ~30 GPa, are illustrated in Fig. 1. The spectral region around the strong triply degenerate T_{2g} mode of diamond, appearing at 1332 cm^{-1} at ambient pressure,[23] is excluded. The background, which gradually increases with

TABLE I. Correlation table of the symmetry groups I_h (molecular symmetry in monomeric C_{60}) and D_{3d} (molecular symmetry in the 2D rhombohedral polymeric C_{60}) (Ref. 14).

I_h	D_{3d}	Splitting ($I_h \rightarrow D_{3d}$)
A_g	A_{1g}	$1 \rightarrow 1$
F_{1g}	$A_{2g}+E_g$	$0 \rightarrow 1$
F_{2g}	$A_{2g}+E_g$	$0 \rightarrow 1$
G_g	$A_{1g}+A_{2g}+E_g$	$0 \rightarrow 2$
H_g	$A_{1g}+2E_g$	$1 \rightarrow 3$
A_u	A_{1u}	$0 \rightarrow 0$
F_{1u}	$A_{2u}+E_u$	$1 \rightarrow 2$
F_{2u}	$A_{2u}+E_u$	$0 \rightarrow 2$
G_u	$A_{1u}+A_{2u}+E_u$	$0 \rightarrow 2$
H_u	$A_{1u}+2E_u$	$0 \rightarrow 2$

pressure, has been subtracted from the experimental spectra. The initial spectrum taken at ~ 0.9 GPa is identical to the spectra reported earlier and exhibits all the typical Raman features of the 2D-R polymer.[14] The spectrum contains some additional peaks related most likely to the presence of oligomers in the material. These peaks are indicated by vertical lines, while arrows indicate weak peaks related to the methanol-ethanol mixture used as the pressure-transmitting medium.

The Raman spectrum of the polymer 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. Table I shows the correlation of the symmetry groups I_h (molecular symmetry of pristine C_{60}) and D_{3d} (molecular symmetry of C_{60} in the 2D-R polymer).[14] Moreover, although the 2D-R polymeric phase retains the inversion center of the C_{60} molecule and the gerade (g) modes are expected to be Raman active, while the ungerade (u) modes infrared active, defects and stresses in the crystal structure of the polymer, as well as natural isotopic ^{13}C substitution, may facilitate the appearance of some u modes in the Raman spectrum of the material. The frequencies and the assignment of the Raman modes of the 2D-R polymer of C_{60} are shown in Table II. The mode assignment refers to the irreducible representations of the C_{60} molecule[24] and follows in general Davydov *et al.*[14] As the pressure increases, the Raman peaks shift to higher energy and their bandwidths gradually increase. The pressure shift of the Raman peaks is accompanied by a gradual redistribution of the intensities among the various Raman modes: the relative intensities of the $H_g(3)$, $H_g(4)$, $G_g(2)$, $F_{1g}(2)$, $H_g(8)$, and $G_g(6)$ modes increase, while the intensities of the $H_g(1)$ and $A_g(1)$ modes decrease. These features in the pressure behavior of the Raman intensities are typical of the various polymeric phases of C_{60} and of some other fullerene-related materials.[13,16] The broadening of the Raman peaks is further enhanced above 10 GPa, most probably due to the solidification of the pressure-transmitting medium leading to pressure gradients.

TABLE II. Phonon frequencies and their pressure coefficients of the initial 2D-R polymeric phase of C_{60} and of the recovered “high-pressure” phase.

2D-R polymeric C_{60}			“High-pressure” phase		
Mode[a]	ω_i (cm^{-1})	$\partial\omega_i/\partial P$ (cm^{-1}/GPa)	Mode	ω_i (cm^{-1})	$\partial\omega_i/\partial P$ (cm^{-1}/GPa)
$H_g(1)$	245	2.3	$\Omega(1)$	228	1.3
$H_g(1)$	267	2.8			
$H_g(1)$	308	3.4			
$H_u(1)$	342	0.6			
$G_u(1)$	406	-0.4	$\Omega(2)$	397	3.1
$H_g(2)$	415	0.2			
$H_g(2)$	438	2.2			
$H_g(2)$	451	0.9			
$A_g(1)$	492	1.1	$\Omega(3)$	470	4.7
$F_{1u}(1)$	520	0.1			
$F_{2g}(1)$	532	0.3			
$F_{1g}(1)$	558	-0.2			
$H_u(2)$	579	0.8			
$H_u(2)$	596	1.4			
$H_u(3)$	640	0.4			
$H_g(3)$	695	-0.5	$\Omega(4)$	705	-0.8
$H_g(3)$	709	-0.6			
$F_{2u}(2)$	712	1.8			
$H_g(3)$	731	-0.2			
$H_g(4)$	749	-0.2			
$F_{2g}(2)$	749	1.8			
$H_g(4)$	767	0.4			
$H_g(4)$	776	0.3			
$F_{2u}(3)$	827	1.0			
$H_u(4)$	856	0.8			
$G_g(2)$	958	5.0	$\Omega(5)$	1025	-1.4
$F_{1g}(2)$	977	5.4			
$H_g(5)$	1078	3.9	$\Omega(6)$	1086	0.3
$H_g(5)$	1109	4.2			
$G_g(3)$	1158	7.2			
$H_g(6)$	1224	5.8			
$H_g(6)$	1230	6.2	$\Omega(7)$	1244	0.6
$H_g(7)$	1385	5.4			
$A_g(2)$	1410	5.6			
$F_{1g}(3)$	1495	3.5			
$H_g(8)$	1554	3.7			
$H_g(8)$	1563	3.9	$\Omega(8)$	1568	4.3
$H_g(8)$	1569	4.3			
$G_g(6)$	1621	3.6			
$G_g(6)$	1627	3.8	$\Omega(9)$	1638	3.3

[a] The mode assignment for the initial 2D-R polymeric phase refers to the irreducible representations of the C_{60} molecule (Ref. 24) and follows in general Davydov *et al.* (Ref. 14).

Drastic changes are first observed near 15 GPa when the Raman spectrum becomes very diffuse and loses its fine structure in all frequency regions. This transformation is preceded by a rapid decrease in the intensity of the $A_g(2)$ pentagonal pinch (PP) mode which vanishes at pressures above 15 GPa. The Raman spectra at $P \geqslant 15$ GPa differ significantly from the spectrum of the 2D-R phase in the pretran-

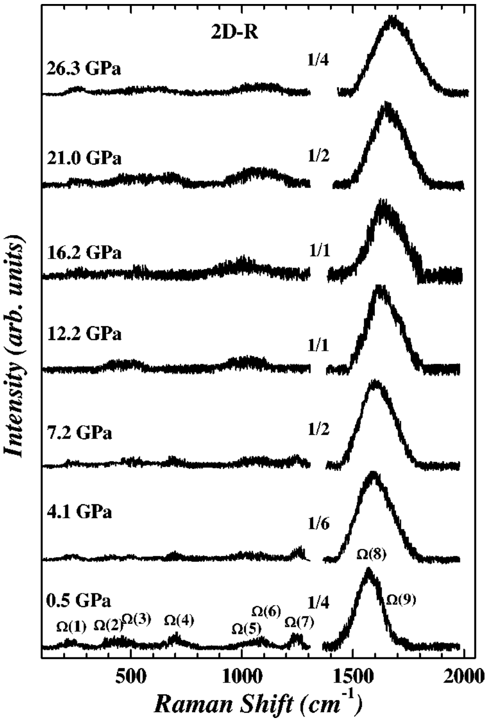

FIG. 2. Raman spectra of the 2D-R polymeric phase of C_{60} at room temperature and various pressures, recorded upon pressure decrease.

sitional pressure range, exhibiting a considerable broadening of the Raman peaks, while the relative intensity distribution among the various phonon bands is preserved. The broad Raman features above $P \geqslant 15$ GPa, designated as $\Omega(1)$–$\Omega(9)$ in the fourth column of Table II (see also the bottom spectrum in Fig. 2), can be tracked back to the initial 2D-R polymeric phase and seem to incorporate the corresponding group of the well-resolved Raman peaks of this material at ambient pressure. The transformed material shows a spatially uniform Raman response over all the surface of the sample, as was evident by probing various spots on the sample. This behavior differs from that observed earlier in the 2D-T polymeric phase of C_{60}.[15]

Figure 2 shows the Raman spectra of the high-pressure phase of the 2D-R polymer upon pressure release. Decrease of pressure from ~30 GPa down to ambient pressure results in the gradual shift of the Raman peaks to lower energies without any observable changes in the Raman intensity distribution. The high-pressure phase remains stable down to ambient conditions. Note that the cycle of the pressure decrease lasted for a long period of time (about one month). The number of the diffuse Raman bands and their positions in the recovered high-pressure phase are different from those in the initial 2D-R phase (see Table I). The diffuse Raman spectra of the recovered material are typical of a highly disordered state, while the spectra taken at various sites of the sample are identical and show the spatial uniformity of the recovered material. The Raman spectra of the high-pressure phase differ significantly from that of amorphous carbon with respect to both the number of peaks and their locations. Our observations from several pressure runs show that the recovered sample is rather stable, not changing at ambient conditions at least for a period of time exceeding one week.

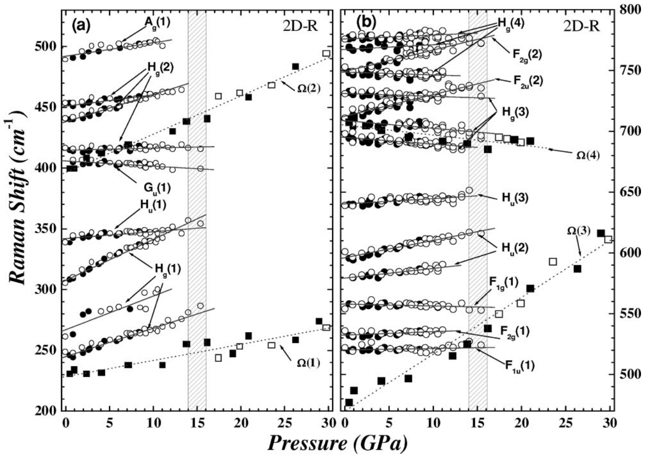

FIG. 3. The pressure dependence of the Raman modes of the 2D-R polymeric phase of C_{60} in the energy regions (a) 200–530 cm^{-1} and (b) 470–800 cm^{-1}. Circles (squares) represent data taken for the 2D-R polymer in the initial (high-pressure) phase. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded area near ~15 GPa denotes the pressure range of the phase transformation.

The pressure dependence of the Raman modes of the 2D-R polymer of C_{60} for the initial (circles) and the high-pressure (squares) phases is shown in Figs. 3(a) and 3(b) in the energy region 200–800 cm^{-1}. The open (solid) symbols denote data taken for upstroke (downstroke) pressure runs. Solid lines are guides to the eye. The mode assignment in these figures is related only to the initial 2D-R polymer and refers, as in Table II, to the irreducible representations of the parent C_{60} molecule (I_h symmetry),[24] following in general the same designation as that in Ref. 14 with minor changes based on the present high-pressure Raman data.

As can be seen from Figs. 3(a) and 3(b) (see also Table I), the pressure-induced shift of the majority of Raman modes of the initial 2D-R polymer is linear and positive, with the exception of six modes with symmetries $G_u(1)$, $F_{1g}(1)$, $H_g(3)$, and $H_g(4)$, which display small negative pressure shifts. The pressure dependence of all Raman modes is reversible with pressure at least up to ~10 GPa, the highest pressure reached during the first experimental pressure run (solid circles in Figs. 3 and 4). The shaded area near 15 GPa indicates the pressure range at which drastic changes in the Raman response take place. The transition to a new high-pressure phase results in the appearance of the diffuse Raman features related most likely to a highly disordered state. The frequencies of the bands in the high-pressure phase were defined with somewhat lower accuracy because of their diffuse nature. Their pressure dependence shows large dispersion and is positive for almost all modes, except for the $\Omega(4)$ mode, which shows a small negative pressure slope.

Figures 4(a) and 4(b) show the pressure dependence of the Raman modes of the 2D-R polymer for the initial (circles) and the high-pressure (squares) phases in the energy region 820–1750 cm^{-1}. All Raman modes of the initial 2D-R polymeric phase in this energy region show positive

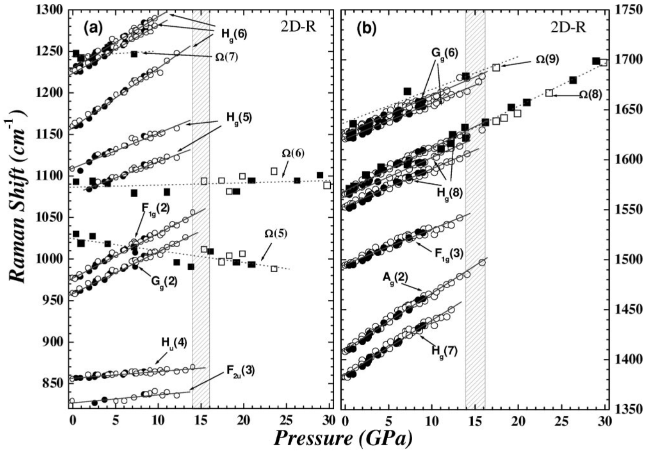

FIG. 4. The pressure dependence of the Raman modes of the 2D-R polymeric phase of C_{60} in the energy regions (a) 820–1300 cm^{-1} and (b) 1350–1750 cm^{-1}. Circles (squares) represent data taken for the 2D-R polymer in the initial (high-pressure) phase. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded area near ~15 GPa denotes the pressure range of the phase transformation.

pressure shift, and their pressure dependence is linear and reversible with pressure at least up to ~10 GPa. The shaded area near 15 GPa also indicates the pressure region where the irreversible transition to the disordered high-pressure phase takes place. The pressure dependence of the diffuse Raman bands in the high-pressure phase is also positive except for the $\Omega(5)$ mode. As it can be seen from Fig. 3 and Fig. 4, the pressure dependence of the $\Omega(8)$ and $\Omega(9)$ modes for the downstroke pressure run is close to the pressure dependence of the corresponding group of modes $H_g(8)$ and $G_g(6)$ of the initial 2D-R polymer located in this frequency region. On the contrary, the pressure dependence of the $\Omega(1)$–$\Omega(7)$ modes differs significantly from that of the group of modes of the initial 2D-R polymer which are located in this frequency region. This may be partially related to relatively high uncertainty in the determination of the frequency positions of the $\Omega(1)$–$\Omega(7)$ bands due to their low intensity in comparison with the more intense $\Omega(8)$ and $\Omega(9)$ modes. The pressure coefficients of the Raman modes in the initial 2D-R phase range between -0.6 and 7.2 cm^{-1}/GPa, while those in the high-pressure phase vary between -1.4 and 4.7 cm^{-1}/GPa. At the same time the pressure coefficients of the Raman modes in pristine C_{60} vary between -4.1 and 9.8 cm^{-1}/GPa. These results are compatible with the fact that the polymerized materials become harder as the degree of polymerization increases.[1,10,25]

Pressure-induced imperfections and structural defects may contribute to the broadening of the Raman bands at higher pressures. In order to explore such a contribution the recovered samples were annealed under various temperature conditions. The Raman spectra of the annealed samples show that the material undergoes some transformation when subjected to a temperature higher than 300 °C. Below this temperature no visible changes in the Raman response of the recovered sample were observed independently of the duration of the annealing procedure. The results of micro-Raman probing of the recovered sample at ambient conditions before and after annealing are shown in Fig. 5. The Raman spectrum of the recovered sample after the pressure cycle, the Raman spectrum of the sample during partial annealing, and the sample after complete annealing at 300 °C are presented in Figs. 5(b)–5(d), respectively, along with the initial spectrum of the 2D-R phase in Fig. 5(a). All spectra were recorded in the energy region 1350–1800 cm^{-1}, which includes the most intense Raman peaks. The Raman spectrum of the completely annealed material is spatially uniform and differs considerably from that of the high-pressure phase as well as from that of the initial 2D-R polymeric phase. This spectrum contains a relatively narrow and intense Raman band near 1464 cm^{-1}, related to the PP mode in the case of a mixture of monomers and dimers of C_{60}, and is similar to the spectra of various annealed polymeric phases of C_{60}.[1,15] Note that the Raman response of the partially annealed sample in Fig. 5(c) contains mainly the diffuse band related to the high-pressure phase, while the prominent Raman bands (shown by arrows) are related to the inclusion of the C_{60} dimers and monomers.

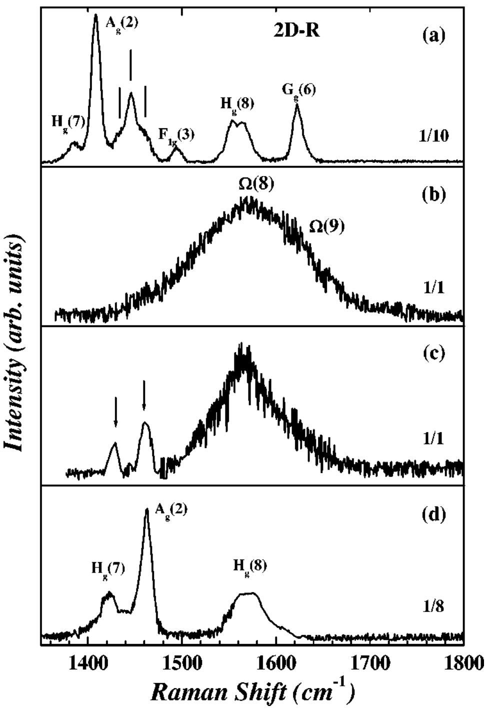

FIG. 5. Raman spectra of the 2D-R polymeric phase of C_{60} and of the recovered sample after high-pressure application in the frequency region 1350–1800 cm^{-1}, recorded at ambient conditions. (a) The initial 2D-R polymeric phase. The vertical lines indicate peaks related to the presence of oligomers in the material. (b) The "high-pressure" phase of the polymer. (c) The Raman spectrum of the "high-pressure" phase during partial annealing. (d) The Raman spectrum of the "high-pressure" phase after being annealed at ~600 K and at ambient pressure. The spectrum is similar to that expected for a sample consisting mainly of C_{60} monomers and dimers.

IV. DISCUSSION

The pressure behavior of the Raman modes provides strong indication that the 2D-R polymeric phase of C_{60} undergoes an irreversible transformation at $P > 15$ GPa. The initial well-resolved Raman spectrum of the 2D-R polymer transforms to a diffuse one that is typical of a disordered phase. The pressure dependence of the phonon modes is reversible with pressure at least up to $\sim$10 GPa as is unambiguously shown by the downstroke pressure data of the first experimental run. Additional experimental runs have shown that the pressure behavior of the Raman modes remains reversible up to $P \leqslant 15$ GPa. At higher pressures, an irreversible transition to a new high-pressure phase takes place. The assignment, frequencies, and pressure coefficients of the Raman modes of the initial 2D-R polymeric phase of C_{60}, shown in Table II, follow in general those given by Davydov *et al.*[14] with minor changes based on the data related to the pressure shift of the Raman modes. Thus, the Raman peak near 712 cm^{-1}, assigned as the $H_g(3)$ mode,[14] has a pressure coefficient of 1.8 cm^{-1}/GPa. This value differs significantly from the other two components of the split $H_g(3)$ mode which have small negative pressure coefficients, -0.4 and -0.6 cm^{-1}/GPa, respectively. On the contrary, the Raman peak near 709 cm^{-1} which has a small negative pressure shift was assigned to an $F_{2u}(2)$ mode.[14] Taking into account the pressure coefficients of these modes, we propose another assignment for the 712 cm^{-1} and 709 cm^{-1} phonons, namely, to $F_{2u}(2)$ and $H_g(3)$ modes, respectively. Similar changes are proposed for the assignment of the 749 cm^{-1} and 767 cm^{-1} Raman bands. Keeping in mind the relatively large pressure coefficient of the 749 cm^{-1} peak, it was assigned to the $F_{2g}(2)$ mode, while the phonon peak at 767 cm^{-1} was assigned to the $H_g(4)$ mode due to its small pressure coefficient reminiscent of the other two components of the split $H_g(4)$ mode.

The important feature in the pressure behavior of the phonon modes is the drastic changes in the region of the PP mode related to the rapid decrease of the intensity of the $A_g(2)$ mode and the enhancement of the neighboring $H_g(8)$ and $G_g(6)$ modes in the pretransitional pressure range. This behavior is reminiscent of an analogous behavior exhibited by these modes in the 2D-T polymeric phase of C_{60} before its further polymerization under high pressure.[12,15,16] The PP mode in pristine C_{60} is related to the in-phase stretching vibration of the five double C═C bonds, which run away from the vertices of each pentagon in the fullerene molecular cage. The frequency of the PP mode in the polymeric fullerenes decreases as the number polymeric covalent bonds per molecular cage increases (the average intramolecular bond stiffness decreases due to the breaking of a number of double intramolecular C═C bonds). Thus, the PP mode in the Raman spectrum of the ‘‘dimeric’’ fullerene shifts to $\sim$1462 cm^{-1} (from 1469 cm^{-1} in pristine C_{60}), and then softens to 1457 cm^{-1} in 1D-O, to 1449 cm^{-1} in 2D-T, and to 1406 cm^{-1} in the 2D-R polymer.[14] The increase of the number of sp^3-like coordinated carbon atoms in the 3D polymer results in further changes in the energy of the PP mode. Namely, the Raman spectrum of the high-pressure phase of the 2D-T polymer contains five strong peaks with the most intense one located at $\sim$1842 cm^{-1}.[12,26] Thus, the breakdown of a large number of double C═C bonds in the high-pressure phase of the 2D-T polymer leads to the quenching of the initial PP mode, and as a result, a number of new Raman peaks appears, possibly related to the stretching vibrations of the remaining isolated double C═C bonds.[27]

The attenuation of the intensity of the PP mode in the pretransitional pressure range is related to the destruction of a number of double C═C bonds followed by subsequent creation of covalent links between molecules belonging to adjacent polymeric sheets in the planar polymers of C_{60}. The high pressure decreases preferentially the distance between the polymeric sheets, but the creation of covalent links is possible only in the case of optimal relative orientations between the molecules belonging to adjacent sheets. A recent x-ray study of the planar polymers of C_{60} at pressure up to 6 GPa has shown that the center-to-center distances of the nearest C_{60} cages between adjacent polymeric sheets in the 2D-R polymer decreases more rapidly than those in the 2D-T polymer. However, the relative molecular orientations and atom-to-atom distances in the 2D-T polymer are more preferable for the formation of covalent bonds between molecules in adjacent polymeric sheets.[28] Thus we may assume that the new bonds in the highly compressed 2D-R polymeric phase of C_{60} are formed in a random way because of the presence of nonoptimal molecular orientations. As a result, the new high-pressure phase exhibits a high degree of disorder characterized by random out-of-plane polymerization. This behavior differs from that of the 2D-T polymeric phase of C_{60} in which the $Immm$ body-centered pseudotetragonal crystal structure[10] provides optimal relative orientations of C_{60} molecules in adjacent sheets and leads to a high degree of regularity in the formation of out-of-plane covalent bonds. This regularity in the covalent bonding is manifested in the Raman features of the high-pressure phase of the 2D-T polymer giving well-resolved and rich Raman spectra.[16,26] However, it is important to note that the Raman response of the pressure-transformed 2D-T polymeric samples is spatially nonuniform: the highly ordered high-pressure phase characterized by well-resolved Raman spectra appears in a number of small islands dispersed in the sample.[15] The rest of the sample is characterized by a rather diffuse Raman spectrum, which is somewhat reminiscent of the high-pressure phase of the 2D-R polymer of C_{60}. This is related to the fact that the 2D-T samples may be inhomogeneous and consist of a mixture of the $Immm$ and $P4_2/mmc$ tetragonal phases since the stacking sequence in the direction perpendicular to the polymeric sheets is strongly dependent on the specific HPHT treatment procedure.[29–31] The stacking disorder is related to the fact that the calculated free energies of the $Immm$ and $P4_2/mmc$ tetragonal phases are very close (the difference between them is about 3%).[32] Note that in the primitive truly tetragonal structure with $P4_2/mmc$ symmetry, the C_{60} molecules in adjacent polymeric sheets do not have optimal relative orientations for the creation of covalent out-of-plane bonds in a regular way.

V. CONCLUSIONS

The diffuse Raman spectrum of the high-pressure phase of the 2D-R polymer may be related to the presence of a disordered cross-linked polymerized phase of C_{60} characterized by random covalent bonding between molecules belonging to adjacent two-dimensionally polymeric sheets of the initial rhombohedral phase. This conclusion is supported by the retention of the fullerene molecular cage in the high-pressure phase, as clearly seen in the Raman spectra of the annealed recovered sample. Another argument in favor of covalent bonding between adjacent polymeric sheets is the similarity in the pretransitional behavior of the PP mode with that of the 2D-T polymeric phase of C_{60}. In addition, the pressure coefficients of the Raman bands in the high-pressure phase of the 2D-R polymer are smaller than those of the initial 2D-R polymer in accordance with the fact that the polymerized materials become harder. The random out-of-plane polymerization of the 2D-R polymer of C_{60} is not in agreement with the theoretical calculations of Burgos *et al.*[11] who predicted regular covalent bonding in 1D and 2D polymers under high pressure.

Finally, we note that a detailed study of the high-pressure behavior of the 2D-R polymeric phase of C_{60} by means of high-resolution *in situ* x-ray-diffraction measurements under pressure up to 30 GPa and/or a x-ray-diffraction study of the recovered sample would be necessary in order to elucidate further the nature of the observed phase transition and the properties of the high-pressure phase. Furthermore, the high-pressure-induced polymeric bond formation is very sensitive to the relative interplane C_{60} cage orientation, therefore the stacking sequence of the initial material might play a role in the structure evolution induced by high-pressure application.

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