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Pressure-induced phase in tetragonal two-dimensional polymeric C_{60}

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The behavior of the phonon modes of the tetragonal phase of the two-dimensional polymerized C_{60} has been studied as a function of pressure, up to 27.5 GPa, at room temperature by means of Raman spectroscopy. Gradual transformation of the material to a new phase was observed in the pressure region 19.0–21.0 GPa. As a result of this phase transformation dramatic changes in the Raman spectrum have been recorded. Namely, the total number of bands was reduced and a number of very strong peaks appeared. The Raman spectrum characteristics provide strong indication that the fullerene molecular cage is retained and therefore the high-pressure phase may be related to a three-dimensionally polymerized C_{60} phase. The high-pressure phase remains stable upon pressure decrease from 27.5 down to 9 GPa. Further release of pressure leads to the destruction of this high-pressure phase to a highly disordered structure whose broad features in the Raman spectrum resemble those of amorphous carbon.

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INTRODUCTION

The behavior of C_{60} fullerite under high pressure has been studied intensively in recent years due to the great interest in its pressure response. A variety of structural transformations of fullerite to amorphous graphite, diamond and ‘‘collapsed’’ fullerite, as well as to other crystalline carbon networks, were reported at the early stages of fullerene studies.[1–4] Later new phases of polymerized fullerites have been synthesized starting from the pristine C_{60} material by the use of high-pressure and high-temperature treatment.[5–7] The various crystal structures of the polymers have been identified clearly as one-dimensional orthorhombic,[6] two-dimensional tetragonal,[6] and two-dimensional rhombohedral phases.[5,6] The polymerization is attained by the so-called $[2+2]$ cycloaddition mechanism via the formation of the four-membered rings between adjacent fullerene molecules.[8,9] The most interesting results are those which led to the three-dimensional polymerization of fullerite,[10,11] a first stage to the synthesis of ultrahard phases.[12]

Recently, Okada *et al.*[13] have shown theoretically the possibility of three-dimensional (3D) polymerization of fullerite using the density-functional theory. They have predicted that the three-dimensionally polymerized fullerite might be formed by the application of uniaxial pressure on the two-dimensional (2D) polymeric tetragonal phase of C_{60}. According to their calculations, polymerization will take place at a value of the lattice constant $c=10.7$ Å, which will be attained at pressure of 20.2 GPa. This polymerization will result in the formation of a stable phase with metallic properties and with $24sp^3$ and $36sp^2$ hybridized C atoms in each C_{60} molecule. To explore this prediction we have studied the pressure response of the two-dimensional tetragonal C_{60} polymer at pressure up to 27.5 GPa by means of Raman spectroscopy using the high-pressure diamond anvil cell (DAC) technique. Our studies have focused on the experimental verification of the theoretical predictions,[13] as well as on the investigation of the pressure behavior of the phonon modes of the 2D polymer of C_{60}.

EXPERIMENTS AND RESULTS

The samples used in the present study were prepared from sublimed 99.99% pure pristine C_{60} powder pressurized in a piston and cylinder device. The material was subjected to pressures in the range 2.3–2.5 GPa at a temperature of about 820 K to obtain 2D polymerized C_{60}.[14] X-ray analysis of the

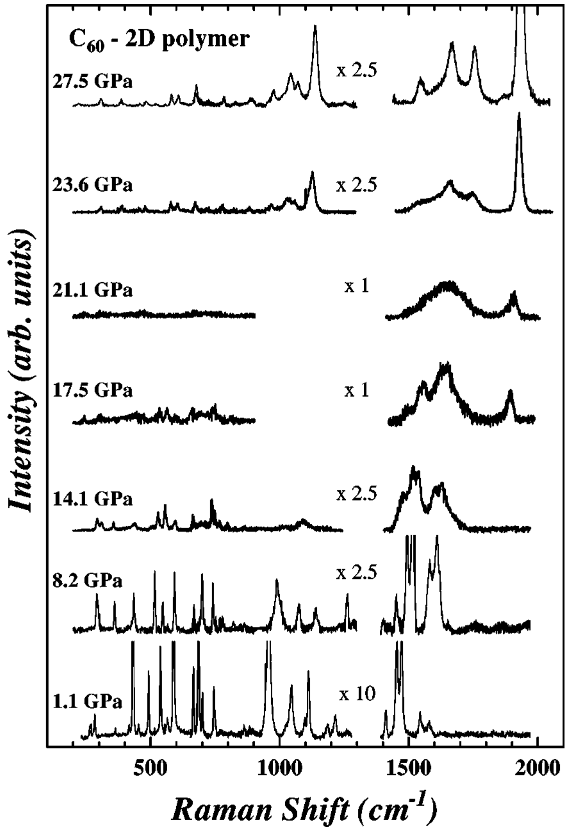

FIG. 1. Raman spectra of the 2D tetragonal C_{60} polymeric phase at room temperature for various pressures up to 27.5 GPa, recorded upon pressure increase.

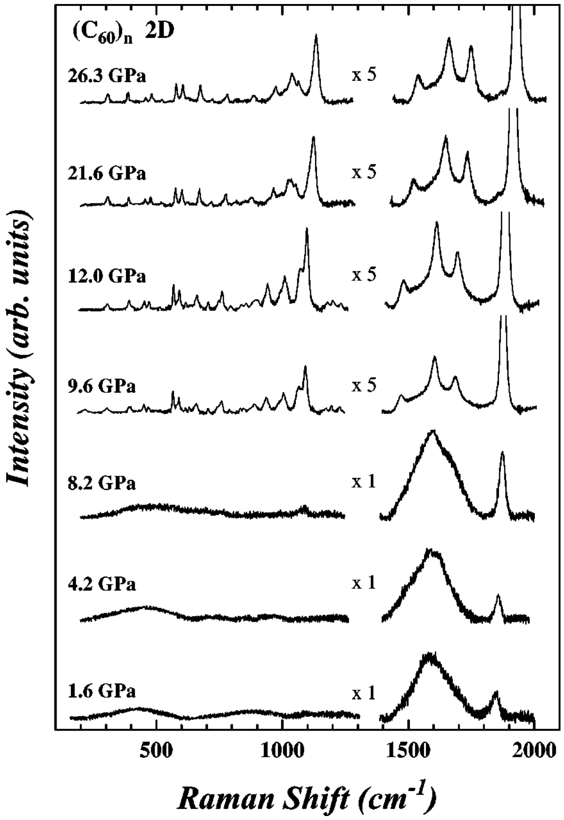

FIG. 2. Raman spectra of the high-pressure phase of the 2D-C_{60} polymer at room temperature for various pressures recorded upon pressure decrease.

samples from the same batch after the high-pressure treatment confirmed that the crystal structure of the polymer is tetragonal (space group *Immm*, $a = 9.082$ Å and $c = 14.990$ Å).[15]

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 was used for excitation. The laser power was varied from 6 to 30 mW measured directly before the cell. Measurements of the Raman spectra at high pressures were carried out using a diamond anvil cell of Mao-Bell type.[16] The 4:1 methanol-ethanol was used as pressure transmitting media and ruby fluorescence technique was used for pressure callibration.[17] The phonon frequencies were calculated by fitting Voigt functions to the experimental Raman spectra of the polymer.

The Raman spectra of the C_{60} two-dimensional tetragonal polymer in the frequency region 200–2000 cm^{-1} and for pressure up to 27.5 GPa are illustrated in Fig. 1. The initial spectrum at 1.1 GPa represents a typical Raman spectrum of this material and is identical with the spectra reported earlier.[18,19] This spectrum is richer in structure than that of the pristine C_{60} due to the splitting of the Raman active five-fold degenerate (H_g) phonon modes or to the activation of silent modes. As the pressure increases the frequencies and the widths of the Raman bands gradually increase. The broadening of the Raman peaks is further enhanced for pressures higher than 13 GPa partly due to the solidification of the pressure-transmitting medium. The most important changes in the Raman spectrum take place in the pressure region between 19 and 21 GPa. In the midpoint of this region the Raman spectrum of the material becomes very weak and structureless that is somehow similar to the Raman spectrum of amorphous carbon. At pressures above 21 GPa a Raman spectrum appears which is probably related with a material transformation to a new phase. Further increase of pressure, up to 27.5 GPa, results in intensity enhancement of most of the observed peaks. The high-pressure Raman spectrum differs significantly from the initial one in respect to the number of peaks, their intensities, and positions. Despite the appearance of very intense peaks the total number of Raman active modes in the final spectrum is almost half of the corresponding number of modes in the lower pressure phase. The high-pressure peaks are located in the frequency region above 1000 cm^{-1}, with the most intense of them being at a frequency of ~ 1850 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} polymer and may be related to the fullerene molecular cage. Nevertheless some of the peaks, located in the high-energy region, do not have an obvious relation with the fullerene molecular cage and may have a different origin.

Figure 2 shows the Raman spectra of the material under pressure release. The decrease of pressure from 27.5 down to 9 GPa does not lead to any observable changes in the Raman

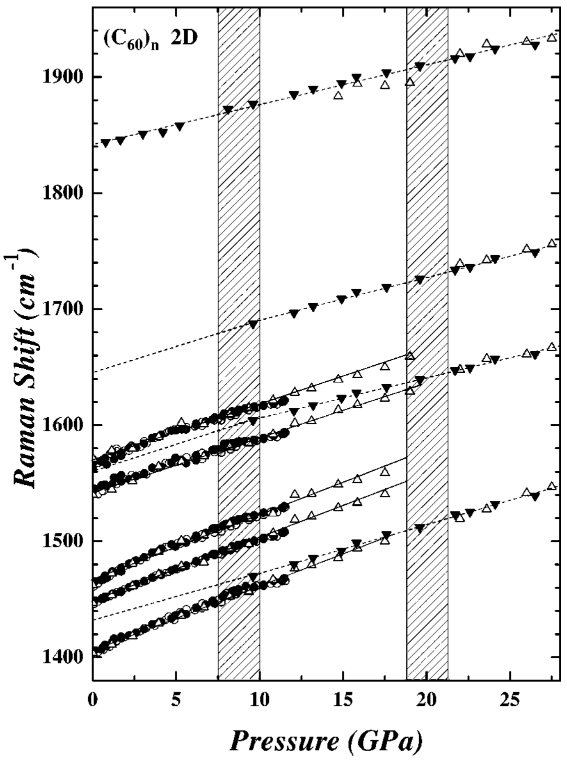

FIG. 3. The pressure dependence of the Raman modes of the tetragonal phase of the 2D-C_{60} polymer, in the frequency region 1380–1960 cm^{-1}. The open (solid) symbols denote data taken for increasing (decreasing) pressure; different symbols represent data from different experimental runs. The dashed areas around 9 ± 1 and 20 ± 1 GPa denote pressure ranges of the phase changes.

intensity distribution and the phase remains stable under pressure release in this high-pressure region. Further decrease of pressure results to a rapid vanishing of all prominent features in the Raman spectrum. At pressures lower than 9 GPa the spectrum loses most of its structure and contains two very broad and weak peaks at ~ 420 cm^{-1} and ~ 1580 cm^{-1}. This spectrum is similar to the Raman spectrum of amorphous carbon. The narrow peak at ~ 1840 cm^{-1} is retained in the spectrum down to a pressure of 1.6 GPa and is most likely related to a trace of the high pressure phase.

Figures 3 and 4 show the pressure dependence of a number of Raman active modes of the C_{60} polymer in the pressure region up to 27.5 GPa. The experimental data, shown by circles and triangles, 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) triangles 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 solid lines represent linear least-square fittings to the experimental data both for increase and release of pressure in the region up to 20 GPa. The dashed lines represent linear least-square fits to the experimental data in the pressure region 20–27.5 GPa for increasing pressure and for the whole region of the down stroke circle. The data obtained in the pressure region up to 12 GPa coincide, within the experimental accuracy, for both pressure runs. The pressure dependence of the phonon modes, up to 12 GPa, does not show any phase transition and is totally reversible with pressure. On the contrary the pressure behavior of phonon modes in the pressure region up to 27.5 GPa is not reversible and shows clearly a phase transition around 20 GPa (dashed area). The slopes of the linear fits of the pressure dependence of Raman frequencies change abruptly near ~ 20 GPa, and a number of additional Raman peaks appear at higher pressure, while some of the peaks disappear. The dashed area near 9 GPa shows the lower limit of stability of the high-pressure phase. At this pressure the Raman spectrum of the material changes dramatically and the majority of the Raman modes disappear. At lower pressures the spectrum contains two very broad peaks and a residual peak of the most intense one, observed in the high-pressure phase at ~ 1840 cm^{-1}. These data indicate that the high-pressure phase may not be stable below ~ 9 GPa under the present experimental conditions and transforms to a state which may be disordered.

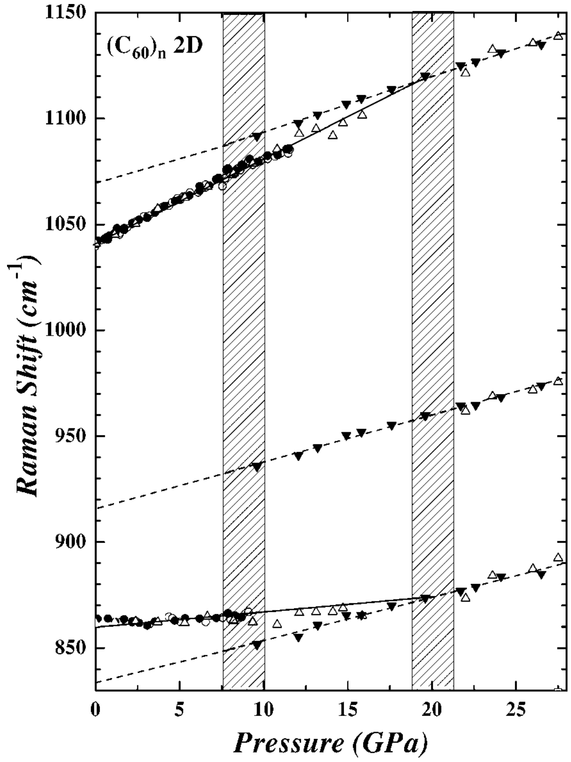

FIG. 4. The pressure dependence of the Raman modes of the tetragonal phase of the 2D-C_{60} polymer in the frequency region 780–1150 cm^{-1}. The symbols have the same meaning as in Fig. 3.

DISCUSSION

The experimental data, obtained by means of high-pressure Raman study of the tetragonal two-dimensional polymeric phase of C_{60}, provide a strong indication that the material undergoes a phase transition at ~ 20 GPa. The specific behavior of the Raman spectrum in the pressure region near the phase transition, namely, the gradual transformation from the initial well defined spectrum to a very diffuse and structureless one followed by a further transformation, at higher pressure, to a spectrum containing sharp and well defined peaks, may be related to the high-pressure induced three-dimensional polymerization of the material. The intermediate diffuse spectrum is associated, in our opinion, with a disordered precursor state of the material when a number of double C=C bonds in the fullerene cage are destroyed in a random way, whereas the polymeric bonds between adjacent molecules are not yet established. The wide pressure region where the material transformation takes place, as well as the irreversibility of the transformation, are related to the fact that the high-pressure induced polymerization is not exactly a phase transition but a solid state chemical reaction.

The reduction of the total number of the Raman active modes in the high-pressure phase indicates a higher symmetry for this phase. The appearance of additional well defined strong Raman modes in this phase of C_{60} may be associated with some changes in the fullerene molecular cage and the creation of out of plane polymeric network resulting in three-dimensional polymerization. For example, the increased number of the sp^3 hybridized carbon atoms per C_{60} molecule may result in the 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 Å in diamond to 1.60 Å in the three-dimensionally polymerized C_{60}.[13] Concerning the most intense Raman peak of the high-pressure phase at 1840 cm^{-1}, it should be mentioned that this cannot be related to a fullerene molecular-cage mode and, most likely, it has different origin. Assuming that the high-pressure phase involves a three-dimensional interfullerene bonding, we may attribute this peak to the stretching vibration of the double C=C bonds, which should be involved in the three-dimensional network of the polymerized material.[20]

Despite the theoretical prediction,[13] the high-pressure phase is not stable and transforms to a different one under pressure release below 9 GPa. The Raman spectrum of the final phase has similarities with that of amorphous carbon. We do not exclude that the latter phase transition may be also related to the second step of the insulator-to-metal phase transition predicted in Ref. 13 as a single phase transition from two-dimensional to three-dimensional polymer of C_{60} with metallic properties. In any case the Raman data obtained in the present study do not contradict this suggestion. We also think that the detailed study of the high-pressure phase, by means of other experimental methods is needed in order to shed light on the nature of this phase. 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 C_{60} at high pressure. This may provide complete information about the structural characteristics of this high-pressure phase, as well as the nature of the final state obtained upon pressure release.

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