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In situ Raman study of path-dependent C_{60} polymerization: Isothermal compression up to 32 GPa at 800 K

A. V. Talyzin and L. S. Dubrovinsky
Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

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In situ Raman study of C_{60} isothermal compression at 800 K and up to 32 GPa was performed using rhombohedral or tetragonal phases as starting materials. Rhombohedral phase showed phase transition to three-dimensional polymers above 10 GPa similar to experiments where isobaric heating was used at pressures 9 to 13 GPa. Tetragonal polymer exhibited significantly stronger stability and can be followed at least up to ~ 15 GPa. Heating up to 800 K of the tetragonal polymer at pressures 6 to 8 GPa confirms that due to geometrical frustrations tetragonal phase remains stable even at $P-T$ conditions where rhombohedral polymer is usually formed from orthorhombic chain polymers.

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Fullerene C_{60} undergoes polymerization at high pressure high temperature (HPHT) conditions. Below 9 GPa and 900 K of several kinds of one- and two-dimensional polymeric phases[1–5] have been obtained: orthorhombic (O), tetragonal (T), and rhombohedral (Rh) (Fig. 1). One- and two-dimensional polymeric phases are well characterized by different techniques including Raman spectroscopy, XRD, etc.[1–10] So far, most of the studies of C_{60} polymerization were performed *ex situ* by treatment of fullerene at HPHT and quenching samples to ambient conditions and only very few *in situ* experiments at HPHT conditions are reported.[6,7,11,12]

Three-dimensionally polymerized superhard fullerites have been reported to form at pressures above 12–13 GPa and temperatures above 800 K.[12–24] The main problem with characterization of "superhard" phases is that they exhibit very few lines in XRD and Raman spectra of these phases are typically almost featureless. One of the most interesting and controversial area in the $P-T$ diagram of C_{60} is about 13 GPa and 800–830 K. Samples obtained at these conditions have been reported harder than diamond by Blank *et al.*,[12–15] but softer than diamond by Brazkin *et al.*[16] Recently, it became clear that not only pressure and temperature, but also some other experimental parameters such as heating time, stress and $P-T$ history can be directly connected to physical properties of synthesized samples.[11,17] It is known that two-dimensional polymerization gives different results depending on the path in $P-T$ space. Increase of temperature followed by pressure ($T-P$ path) favor formation of tetragonal phase, while pressure increase followed by heating ($P-T$ path) applied for the same final $P-T$ conditions (about 2.2 GPa and 870 K) results in a synthesis of mixture of tetragonal and rhombohedral polymers.[4,9,25] It can be proposed that the $T-P$ path gives an advantage to polymerization in the (001) direction of the original fcc structure of C_{60}, while the $P-T$ path favor polymerization in the (111) direction. So far all studies of the 3D polymerization have been performed only using pressurizing followed by heating ($P-T$ path). Due to the experimental difficulties the $T-P$ path has never been tested for pressure regions above 6 GPa.

In the present study the $P-T$ region at about 13 GPa and 800 K was approached from the lower pressure at isothermal conditions starting either from (mostly) rhombohedral phase, or from (mostly) tetragonal phase. Phase transformations were followed by modifications of Raman spectra recorded *in situ* during the $P-T$ treatment. We also studied a possibility of direct transformation from tetragonal to rhombohedral polymeric phase at HPHT conditions.

A powder sample of C_{60} (99.9% purchased from MER corporation) together with a small piece of ruby were loaded into a specially designed type diamond anvil cell[26] with 250 μm flat culets without pressure-transmitting media. Pressure was measured using the ruby fluorescence scale corrected for temperature effects.[27] Uncertainty in pressure determination was within 1 GPa, and in temperature, measured with K-type

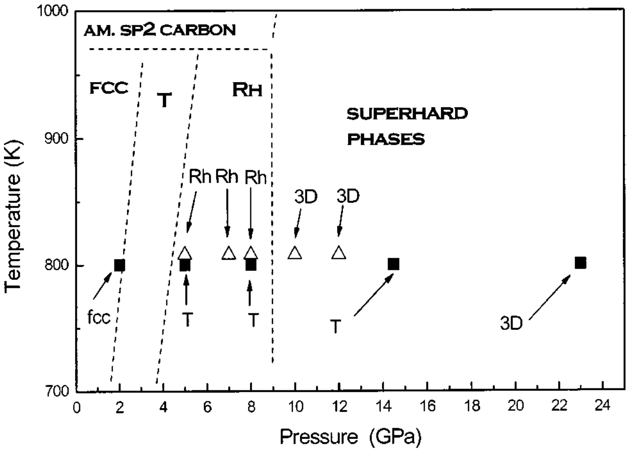

FIG. 1. Phases observed during *in situ* high pressures and temperatures experiments with tetragonal (black squares) and rhombohedral (open triangles) phases as starting materials. Tetragonal phase was presynthesized in piston-cylinder apparatus by heating C_{60} at 2.5 GPa and 800 K for 60 min (and consequently purified by decompression at 800 K from 8 to 2 GPa followed by pressurizing at constant temperature back to 8 GPa), while rhombohedral phase was synthesized *in situ* by heating pristine C_{60} at 800 K and 5 GPa. Phase relations shown by lines are from Refs. 4, 5, and 15. Symbols "fcc," "T," "Rh," "3D" (monomeric, tetragonal, rhombohedral, and three-dimensional polymers, respectively) correspond to polymeric phases observed for these two experiments at every experimental point where Raman spectra were recorded.

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TABLE I. Signature peaks for tetragonal and rhombohedral polymers.

Assignment	T, 8 GPa, 800 K	T, 6 GPa, RT	Rh, 8 GPa, 800 K	Rh, 8 GPa RT
Hg(1)	278	288		
Hg(2)			415	420
Hg(2)	428	433		
Hg(3),Hg(4)?			725	725
Hg(3),Hg(4)?	739	741		

thermocouple, ±10 K. Raman spectra were recorded *in situ* during the $P-T$ treatment, using LabRam spectrometer equipped with He–Ne laser operating at 632 nm and with resolution 2 cm^{-1}. Low laser power was used to avoid photopolymerization. The pressure gradient at the highest pressure (32 GPa) was about ±1 GPa within 100 μm of the central part of the sample. Raman spectra were always recorded in the central part of the sample in approximately the same spot close to the ruby chip.

Two experiments were aimed on observation of 3D polymerization by isothermal compression at 800 K using 2D polymeric phases as precursors. In the first experiment a rhombohedral phase was synthesized *in situ* prior compression at 8 GPa and 800 K. In the second run, sample of tetragonal phase synthesized in piston-cylinder apparatus by heating C_{60} at 2.5 GPa and 800 K for 60 min was used.

During the heating, the temperature was allowed to stabilize at every 100 K for 10–20 min and Raman spectra were recorded using acquisition times of 5 to 30 min. Some measurements with shorter exposure were also carried out at intermediate temperatures. Experimental points taken at 800 K and pressure range 2 to 32 GPa are shown in Fig. 1.

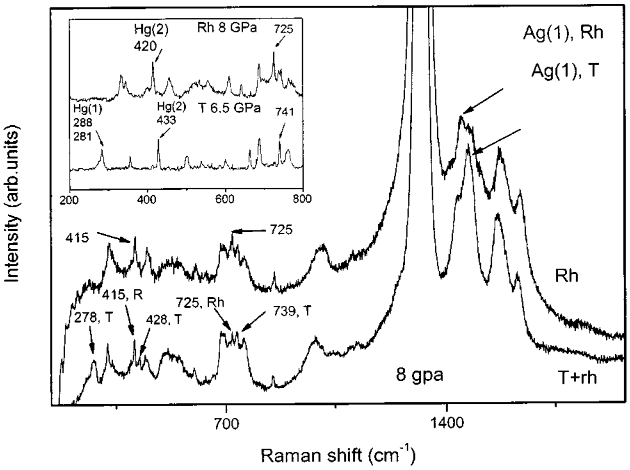

FIG. 2. Raman spectra of rhombohedral (Rh) and (mostly) tetragonal phase (T) at 800 K and 8 GPa. Inset shows Raman spectra of the rhombohedral and tetragonal polymers recorded at 293 K at 8 and 6.5 GPa, respectively. Numbers are given for positions of "signature peaks."

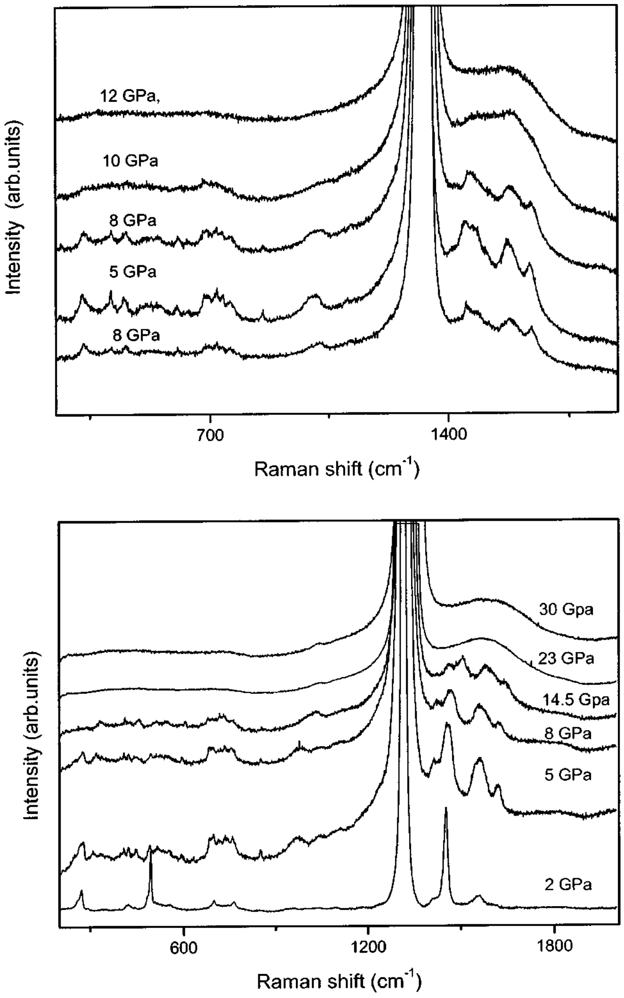

FIG. 3. Raman spectra recorded *in situ* during isothermal compression of Rh (a) and T (b) polymeric phases at 800 K.

In previous studies[4–7] Ag(2) Raman peak position have been used for identification of different polymeric phases. However, at elevated pressure and temperature the assignment of Ag(2) is difficult due to the $P-T$ dependent shift and strong overlapping of peaks from different polymeric phases. Contrary, positions of peaks below 1100 cm^{-1} are almost independent on pressure and temperature in the studied $P-T$ range. Table I and Fig. 2 show a number of characteristic peaks of both Rh and T phases and their possible assignment based on literature data[6,7,28] and our own observations.

Figure 2 shows Raman spectra of two samples recorded at 800 K and 8 GPa prior to the compression aimed on 3D polymerization. Analysis of these spectra proves that the first sample (experiment 1) consists of mostly rhombohedral phase, while the second (experiment 2) consists of tetragonal polymer with some small amount of the rhombohedral phase (see Table I for typical peaks used for phase identification).

Results of two experiments with isothermal compression at 800 K for T and Rh phases are summarized in Fig. 1 and compared with previously reported $P-T$ diagram.[4,5,15] Isothermal compression of Rh phase from 5 to 12 GPa resulted in drastic changes of Raman spectra [Fig. 3(a)]. Already at 10 GPa the spectrum of Rh phase degraded into few broad features. At 12 GPa the Raman spectrum of this sample looks identical to the spectra of reportedly "superhard" phases. This spectrum can be attributed to either a 3D polymer or amorphous carbon phase formed as a result of fullerene cage collapse.[12–24]

Phase transformations of tetragonal phase during compression from 8 GPa to 30 GPa at 800 K appeared to be different from the similar experiment with rhombohedral phase [Fig. 3(b)]. First of all, the sample remained in mostly tetragonal phase after heating at 8 GPa from room temperature to 800 K. We did not observe a direct transformation from tetragonal to rhombohedral phase during the heating. Some amount of the Rh phase, which can be recognized in the Raman spectrum recorded from this sample at 800 K and 8 GPa, originates from a transformation of chain polymers, which were present in the starting material as an impurity.

Better purity of the tetragonal phase was achieved by decompression at 800 K from 8 to 2 GPa followed by pressurizing at constant temperature back to 8 GPa [Figs. 2 and 3(b)]. The Raman spectrum recorded at 2 GPa is typical for monomeric C_{60} [Fig. 3(b)]. In agreement with previous studies,[4,25] the sample prior compression at 800 K to 8 GPa consisted mostly of tetragonal phase, but still contained admixture of some small amount of the Rh phase (Fig. 2). Compression of this sample at 800 K up to 32 GPa resulted in a transformation (suggestively 3D polymerization) similar to the previous sample (where Rh phase was compressed at 800 K) but at much higher pressure. It was found that tetragonal phase exhibits a remarkable stability against a compression. At 15 GPa all typical peaks from this phase still can be clearly recognized in the Raman spectrum and even at 23 GPa some traces from these peaks can be observed. This is strongly different from the first experiment [see Fig. 3(a)] where peaks from the rhombohedral phase disappeared already at 10 GPa. As can be seen in Fig. 1, results of experiment with Rh phase are in a good agreement with previously constructed $P-T$ diagrams, while tetragonal phase shows remarkably stronger stability against a compression.

The samples recovered after both experiments exhibited Raman spectra typical for so-called ‘‘superhard phases’’ with only two broad peaks.[5,11,13–16] No new 3D polymeric phases similar to those reported by Meletov *et al.*[29,30] were observed in our experiments.

Interesting results were also obtained by analysis of evolution of Raman spectra during the heating of the tetragonal polymer from 293 to 800 K at 6–8 GPa. Although known $P-T$ diagrams[4,5,15] suggest that upon heating at those pressures the tetragonal phase should directly convert into the rhombohedral one, we did not observe such transformation. While the chain polymer contaminated initial sample of the tetragonal phase transforms into the rhombohedral phase at about 650–700 K, the tetragonal phase remains unchanged even after hours of heating at 8 GPa and 800 K.

It is known that the tetragonal phase is formed by polymerization in the (001) plane of initial fcc structure of C_{60}, while rhombohedral phase forms due to polymerization in the (111) direction.[4,9,25] Due to geometrical frustrations the rhombohedral phase cannot be obtained directly from the tetragonal without breaking of some polymeric bonds. So, the possible scenarios of behavior of tetrahedral phase at high pressure and temperature could be (a) depolymerization of a tetragonal polymer on chains and a consequent polymerization in the (111) direction (direct transformation to rhombohedral phase); (b) tetragonal phase remains stable even at $P-T$ conditions where a rhombohedral polymer is usually formed from orthorhombic chain polymers; and (c) tetragonal phase polymerized in the (111) direction of initial fcc C_{60} structure and directly transforms into 3D polymer(s). Our experiments show that at pressure from 6 to 15 GPa, and high temperature behavior of the tetragonal phase, follows the second scenario and at even higher pressure tetragonal phase starts to transform into presumably a 3D polymer [scenario (c)]. Our experiments also clearly demonstrate that kinetic $P-T$ phase diagram (or ‘‘experimental maps’’) of C_{60} (Fig. 1) depends on both the starting material and the pressure-temperature path.

In fact, all $P-T$ diagrams presented in the literature[4,5,15] were constructed using the $P-T$ path (isobaric heating) and the present work shows that the $P-T$ diagram constructed using the $T-P$ path (isothermal pressurizing) is remarkably different. This fact once more emphasizes that the true phase diagram of C_{60} polymers does not exist (because C_{60} is a metastable form of carbon), only ‘‘experimental maps’’ or ‘‘kinetic $P-T$ diagrams’’ can be constructed. It is clear that many more isothermal pressurizing experiments at different temperatures are required to construct the ‘‘$T-P$ path kinetic phase diagram.’’ Nevertheless, at least one strong difference is clear from the presented study. In contrast to presently available $P-T$ diagrams, on the ‘‘$T-P$ path phase diagram’’ the most stable at 800 K and 6–15 GPa pressure is not the rhombohedral, but the tetragonal polymeric phase.

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[1] M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Bethoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).

[2] A. M. Rao, P. C. Eklund, J.-L. Hodeau, L. Marques, and M. Nunez-Regueiro, Phys. Rev. B **55**, 4766 (1997).

[3] V. A. Davydov, V. Agafonov, H. Allouchi, R. Ceolin, A. V. Dzyabchenko, and H. Szwarc, Synth. Met. **103**, 2415 (1999).

[4] V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. M. Senyavin, R. Ceolin, H. Szwarc, H. Allouchi, and V. Agafonov, Phys. Rev. B **61**, 11936 (2000).

[5] B. Sundqvist, Adv. Phys. **48**, 1 (1999).

[6] A. V. Talyzin, L. S. Dubrovinsky, T. Le Bihan, and U. Jansson, J. Chem. Phys. **116**, 2166 (2002).

[7] A. V. Talyzin, L. S. Dubrovinsky, T. Le Bihan, and U. Jansson, Phys. Rev. B **65**, 245413 (2002).

[8] T. Wågberg, P.-A. Persson, and B. Sundqvist, J. Phys. Chem. Solids **60**, 1989 (1999).

[9] R. Moret, P. Launois, T. Wågberg, and B. Sundqvist, Eur. Phys. J. B **15**, 253 (2000).

[10] T. Wågberg, P. Jacobsson, and B. Sundqvist, Phys. Rev. B **60**, 4535 (1999).

[11] A. V. Talyzin, L. S. Dubrovinsky, M. Oden, T. Le Bihan, and U. Jansson, Phys. Rev. B **66**, 165409 (2002).

[12] T. Horikawa, K. Suito, M. Kobayashi, and A. Onodera, Phys. Lett. A **287**, 143 (2001).

[13] V. D. Blank, S. G. Buga, G. A. Dubitsky, N. R. Serebryanaya, M. Yu. Popov, and B. Sundqvist, Carbon **36**, 319 (1998).

[14] V. D. Blank, S. G. Buga, N. R. Serebryanaya, V. N. Denisov, G. A. Dubitsky, A. N. Ivlev, B. N. Martin, and M. Yu. Popov, Phys. Lett. A **205**, 208 (1995).

[15] V. D. Blank, S. G. Buga, N. R. Serebryanaya, G. A. Dubitsky, S. N. Sulyanov, M. Yu. Popov, V. N. Denisov, A. N. Ivlev, and B. N. Martin, Phys. Lett. A **220**, 149 (1996).

[16] V. D. Blank, S. G. Buga, N. R. Serebryanaya, G. A. Dubitsky, R. H. Bagramov, M. Yu. Popov, V. M. Prokhorov, and S. A. Sulyanov, Appl. Phys. A: Mater. Sci. Process. **64**, 247 (1997).

[17] V. V. Brazkin, A. G. Lyapin, S. V. Popova, Yu. A. Klyuev, and A. M. Naletov, J. Appl. Phys. **84**, 219 (1998).

[18] N. R. Serebryanaya, L. A. Chernozatonskii, Solid State Commun. **114**, 537 (2000).

[19] L. Marques, M. Mezouar, J.-L. Hodeau, M. Nunez-Regueiro, N. R. Serebryannaya, V. A. Ivdenko, V. D. Blank, and G. A. Dubitsky, Science **283**, 1720 (1999).

[20] E. Burgos, E. Halac, R. Weht, H. Bonadeo, E. Artacho, and P. Ordejon, Phys. Rev. Lett. **85**, 2328 (2000).

[21] F. Moshary, N. H. Chen, I. F. Silvera, C. A. Brown, H. C. Dorn, M. S. de Vries, and D. S. Bethune, Phys. Rev. Lett. **69**, 466 (1992).

[22] C. S. Yoo and W. J. Nellis, Chem. Phys. Lett. **198**, 379 (1992).

[23] A. V. Talyzin, L. S. Dubrovinsky, M. Oden, and U. Jansson, Diamond Relat. Mater. **10**, 2044 (2001).

[24] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **83**, 1986 (1999).

[25] V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. Agafonov, H. Allouchi, R. Ceolin, A. V. Dzyabchenko, V. M. Senyavin, and H. Szwarc, Phys. Rev. B **58**, 14786 (1998).

[26] N. A. Dubrovinskaia and L. S. Dubrovinsky, Rev. Sci. Instrum. (in press).

[27] S. Rekhi and L. S. Dubrovinsky, High Temp. - High Press. **31**, 299 (1999).

[28] A. V. Talyzin and L. S. Dubrovinsky, High Temp. - High Press. **35/35**, 47 (2003).

[29] K. P. Meletov, J. Arvanitidis, I. Tsilika, S. Assimopoulos, G. A. Kourouklis, S. Ves, A. Soldatov, and K. Prassides, Phys. Rev. B **63**, 054106 (2001).

[30] K. P. Meletov, J. Arvanitidis, I. Tsilika, S. Assimopoulos, G. A. Kourouklis, S. Ves, B. Sundqvist, and T. Wagberg, Chem. Phys. Lett. **341**, 435 (2001).